

THE ELECTRICAL PROPERTIES OF FLAMES AND OF INCANDESCENT SOLIDS

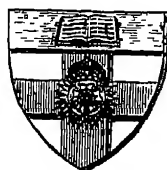
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THE
ELECTRICAL PROPERTIES
OF FLAMES
AND OF
INCANDESCENT SOLIDS

BY
HAROLD A. WILSON

D SC (LONDON), M A , F R S , F R S C.

FORMERLY FELLOW OF TRINITY COLLEGE, CAMBRIDGE, AND PROFESSOR OF
PHYSICS IN KING'S COLLEGE, UNIVERSITY OF LONDON, MACDONALD
PROFESSOR OF PHYSICS IN MCGILL UNIVERSITY, MONTREAL



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PREFACE

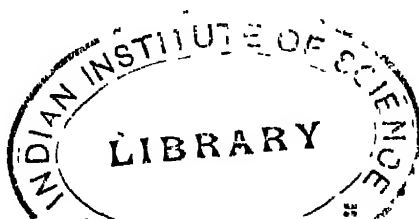
THIS book is intended to give a concise but fairly complete account of recent researches on the electrical properties of incandescent bodies and of flames. I have attempted to present the mathematical theory required in as simple a form as possible, without loss of accuracy, and to make estimates of the reliability of some of the measurements described. Some matter not hitherto published is contained in the book

H. A. W.

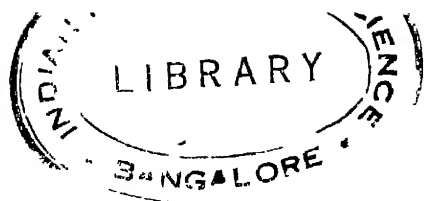
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ELECTRICAL PROPERTIES OF FLAMES

CHAPTER I

INTRODUCTION

THAT flames conduct electricity and that hot bodies lose an electrical charge and various other associated facts have been known for more than a century, but it is only during the last twenty years that the electrical properties of bodies at high temperatures have been systematically investigated

The earlier observations are mostly of a purely qualitative character, and the conditions of the experiments described not sufficiently definite for them to be of much use for an accurate comparison between theory and experiment.

The development of the ionic theory of the electrical properties of gases by Sir J. J. Thomson led to numerous experimental investigations, which naturally included an examination of the electrical properties of flames and hot solids in the light of the new theory. In consequence a great increase in our knowledge of the relations between matter and electricity at high temperatures has taken place and the ionic theory has become firmly established in this field.

The following pages contain an account of many of the more recent investigations on the electrical properties of hot bodies and flames, especially of such as are of a quantitative character giving results capable of accurate comparison with theory.

Elster and Geitel¹ made a great many observations on the charge acquired by an insulated plate put near hot wires in different gases at various pressures.

¹ *Wied. Ann.* 1882, 1883, 1884, 1885, 1887, 1889.

Sir J. J. Thomson¹ measured the conductivity of many gases and vapours of salts and metals between platinum electrodes at a bright red heat. Gases and vapours which dissociate he found conduct very much better than those which do not

Sir J. J. Thomson² in 1899 determined the ratio of the charge e to the mass m of the negative ions emitted by an incandescent carbon filament in hydrogen at a low pressure, and found it equal to about 10^7 , which is the value of e/m for electrons.

McClelland³ examined gases which had been drawn past a hot platinum wire and showed that they contained positive and negative ions. The velocity of these ions due to an electric field he found was very small and smaller the hotter the wire.

The writer⁴ examined the variation of the current from hot platinum in air with the temperature, and from the rate of variation calculated the energy rendered latent by the formation of the ions at the surface of the platinum.

Rutherford⁵ measured the velocity of the ions emitted by hot platinum in air and found that the ions had a considerable range of velocities. The average velocity increased with the temperature.

O. W. Richardson⁶ examined the current from hot platinum in a vacuum and explained its variation with the temperature by supposing that the electrons in the metal, to which its conductivity is due, escape at high temperatures. Richardson's theory is now well established as the result of many investigations by himself and others.

Giese⁷ investigated the electrical properties of the gases coming from flames and explained many of them on the ionic theory.

McClelland⁸ determined the velocities of the ions in gases drawn from flames and found them to vary from 0.23 cm. per

¹ *Phil. Mag.* V. 29, pp. 358, 441, 1890.

² *Phil. Mag.* V. 48, p. 547, 1899.

³ *Proc. Camb. Phil. Soc.* vol. x. p. 241, 1900.

⁴ *Phil. Trans. A.* vol. 197, p. 415, 1901.

⁵ *Physical Review*, vol. xiii, December 1901.

⁶ *Proc. Camb. Phil. Soc.* vol. xi p. 286, 1902.

⁷ *Wied. Ann.* vol. xvii. pp. 1, 236, 519, 1882; vol. xxxviii. p. 403, 1889.

⁸ *Phil. Mag.* V. 46, p. 29, 1898.

sec. for one volt per cm. near the flame to 0.04 cm. per sec. some distance away.

Arrhenius¹ in 1891 investigated the conductivity of flames containing salt vapours, and found that the conductivity due to salts of the alkali metals increases rapidly with the atomic weight of the metal.

Arrhenius' results were confirmed and extended by Smithells, Dawson, and the writer²

The writer³ measured the velocity of the ions in flames, and showed later⁴ that Faraday's laws of electrolysis apply to alkali salt vapours at high temperatures.

The investigations just mentioned are some of the first of those in which definite quantities were measured. Most of the above and subsequent researches are described more fully in the following chapters.

A full account of the old experiments is given in Wiedemann's *Electricität*, Bd IV B. Sir J. J. Thomson, in *Conduction of Electricity through Gases*, gives a summary of the most important observations made by the earlier experimenters and references to their papers.

I have not discussed the numerous observations which have been made on gases drawn from flames or from the neighbourhood of hot wires. These observations show that ions are present in such gases and their velocities have been found. Also I have not given any account of the numerous observations on the deflection of flames by electric and magnetic fields.

¹ *Wied. Ann.* vol. xliii. p. 18, 1891.

² *Phil. Trans. A.* vol. 193, p. 89, 1899.

³ *Phil. Trans. A.* vol. 192, p. 499, 1899.

⁴ *Phil. Trans. A.* vol. 197, p. 415, 1901.

CHAPTER II

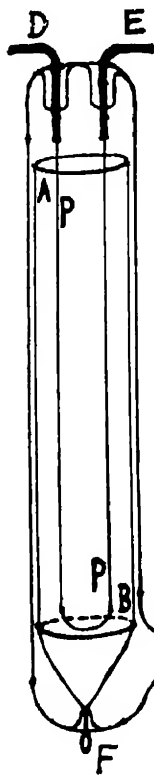
THE DISCHARGE OF NEGATIVE ELECTRICITY BY HOT PLATINUM IN A VACUUM

WHEN a negatively charged clean wire of pure platinum is raised to a high temperature in a vacuum, it is found to lose its charge. If the negative terminal of a battery is connected to the hot wire, and the positive terminal to a conductor near the wire,

a continuous current passes between the conductor and the wire through the vacuum, but if the connections of the battery are reversed little or no current is obtained. The current is only obtained when the wire is hot, so that it is clear that it consists of negative electricity emitted by the wire. The current obtained is about 10^{-8} to 10^{-7} of an ampere per sq cm. of platinum surface, at a temperature of about 1600°C . Much larger currents than this may be obtained if impurities, such as hydrogen and alkali metal salts, are present in the platinum, even in minute quantities. The current increases rapidly with the temperature of the wire.

The above statements can be verified with the apparatus shown in Fig. 1. A loop of pure platinum wire PP is suspended inside a glass tube about 2 cms. in diameter and 12 cms. long.

The ends of the loop are attached to two stout platinum wires DE sealed through the upper end of the tube. A cylinder of platinum foil AB surrounds the loop and is connected to wires sealed through the lower end of the tube at F. A side tube leads



to a mercury pump capable of reducing the pressure below 0.001 mm. of mercury. The loop may be of wire 0.2 mm., and the wires DE about 1 mm. in diameter. Before sealing the side tube to the pump, the apparatus is washed with boiling nitric acid and distilled water.

The loop is heated by passing a current through it, and its resistance is found by making it one of the arms of a Wheatstone's bridge. The temperature of the loop is obtained from its resistance. The current between the loop and the cylinder is measured with a galvanometer. To get rid of gases evolved by the apparatus when the wire is heated, it is best to admit air to atmospheric pressure and pump it out several times while the wire is kept at about 1600° C. If these precautions are taken and a good vacuum obtained, the current from the wire will be found to be of the order of magnitude stated, and will remain fairly constant. The use of charcoal and liquid air greatly facilitates the obtaining of a good vacuum.

According to the ionic theory, we should expect the negative electricity emitted by the wire to be carried by charged atoms, or to consist simply of free electrons. The ratio of the charge (e) to the mass (m) of the negative ions emitted by a hot carbon filament was determined by Sir J. J. Thomson in 1899.¹ Two parallel aluminium plates were arranged in a vessel which could be exhausted. A small incandescent lamp filament was fixed between the plates and close to one of them. The plate near the filament was negatively charged, and the current carried by the negative ions from the filament to the other plate was measured. When magnetic field was produced parallel to the plates, this current was diminished if the field was greater than a definite value depending on the potential difference and distance between the plates. From the values of these quantities the ratio e/m was calculated, and found to be about 9×10^6 , which agrees within the errors of experiment with the value of e/m for cathode ray or negative electrons. For the negative electricity emitted by glowing Nernst filament Owen² found $e/m = 6 \times 10^6$, and for the

¹ *Phil. Mag.* V. 48, p. 547, 1899

² Owen, *Phil. Mag.* VI. 8, p. 230, 1904

emitted by hot lime Wehnelt¹ found $e/m = 1.4 \times 10^7$ O. W. Richardson² has recently measured e/m for the negative electricity emitted by hot platinum itself, and finds it equal to about 1.5×10^7 . Thus it is clear that the negative electricity is emitted as free negative electrons. The emission of these electrons by many quite different substances at high temperatures affords a convincing proof that they are a common constituent of all forms of matter.

In discussing the discharge of electricity from hot bodies, it is convenient to adopt a special name for the current carried by the electrons or ions emitted. Following Prof O. W. Richardson, I shall call this current the thermionic current, and the ions carrying it thermions.

The thermionic current obtained in a good vacuum is independent of the potential difference, provided this is greater than a few volts. If the P.D. is very small, some of the electrons which escape diffuse back to the wire, so that the current is smaller.

The maximum current is usually called the saturation current.

The variation of the thermionic current from hot platinum in a vacuum with the temperature of the platinum was first investigated by O. W. Richardson,³ who at the same time put forward an elegant theory to account for it, which is now firmly established.

The variation of the thermionic current with the temperature is shown in Fig. 2, given by Richardson (*loc. cit.*).

If i denotes the saturation thermionic current per sq. cm. of platinum surface, and θ the absolute temperature, then Richardson found $i = A\theta^{1/2}e^{-Q/2\theta}$, where A and Q are constants. This formula represents the curves shown in Fig. 2 very well.

The following table, taken from a paper by the writer,⁴ shows the accuracy with which Richardson's formula represents the

¹ Wehnelt, *Ann. d. Phys.* vol. xiv. p. 425, 1904

² *Phil. Mag.* (6) vol. xvi. p. 740, 1908. *Ibid.* (6) vol. xx. p. 545, 1910.

³ *Proc. Camb. Phil. Soc.* vol. xi. p. 286, 1902. *Phil. Trans.* vol. 201, p. 516, 1903

⁴ H. A. Wilson, *Phil. Trans.* vol. 202, p. 243, 1903.

thermionic current The calculated currents are those given by the equation $i = 6.9 \times 10^7 i_0 e^{-181000/2\theta}$.

Temperature	Current per sq. cm. found.	Current calculated.
°C		
1375	1.57×10^{-8}	1.49×10^{-8}
1408.5	3.43 "	3.33 "
1442	7.46 "	7.18 "
1476	15.2 "	15.3 "
1510.5	32.3 "	31.8 "
1545	63.8 "	64.5 "
1580	128 "	128.5 "

According to Richardson's theory the electrons which escape from hot bodies are those which are contemplated in the electron

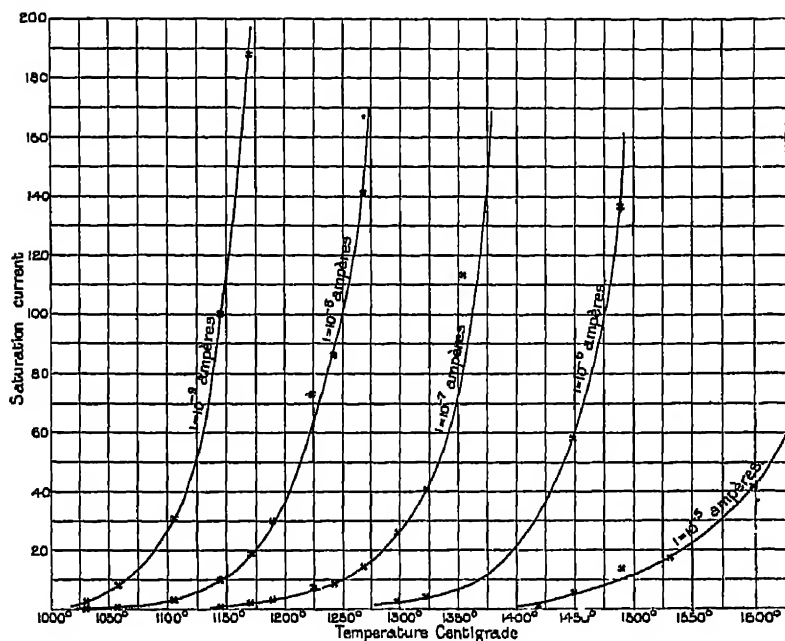


FIG. 2

theory of metallic conductivity and heat radiation. A metal is supposed to contain a large number of free negative electrons, which move about inside it, colliding with the metallic atoms just

as the molecules of a gas collide with each other on the kinetic theory of gases. The negative charge (q) carried by all the free electrons in one cc of the metal is equal to the positive charge on the atoms in one cc. The electrons between collisions are supposed to move freely, and their mean kinetic energy of translation is taken to be equal to that of a gas at the temperature of the metal. The distribution of velocities among the electrons is given by Maxwell's well-known law, just as in the case of a gas.

At the surface of the platinum it is convenient to suppose the existence of an electrical double layer in accordance with the usual theory of contact potential differences. In this double layer the negative charge must be on the outside. Let the fall of potential across the double layer be φ , so that an electron in escaping from the platinum through the layer must do work φe ergs. Consequently, if the velocity of an electron on entering the layer is v_1 perpendicular to the layer, and v_2 when it gets out, we have

$$\frac{1}{2}m(v_1^2 - v_2^2) = \varphi e$$

In going through the layer we suppose the velocity components parallel to the layer to be unchanged

Let n denote the number of free electrons per cc in the metal. Then, according to Maxwell's law, the number dn per cc. which have velocity components perpendicular to the surface of the platinum lying between v and $v + dv$ is given by

$$dn = n \left(\frac{q}{\pi} \right)^{\frac{1}{2}} e^{-qv^2} dv$$

where $q = 3/2\bar{v}^2$ and \bar{v}^2 denotes the mean value of the square of the resultant velocity of an electron.

Hence, the number of electrons entering unit area of the double layer per second is

$$\int_{v=0}^{v=\infty} n \left(\frac{q}{\pi} \right)^{\frac{1}{2}} e^{-qv^2} dv$$

Of these, only those for which v is greater than $\sqrt{2\varphi e/m}$ will have enough energy to get through the double layer, so that the number escaping per second is

$$n \left(\frac{q}{\pi} \right)^{\frac{1}{2}} \int_{v=\sqrt{2\varphi e/m}}^{\infty} e^{-qv^2} dv = \frac{n}{\gamma} e^{-3\varphi e/m} = \frac{1}{e}$$

DISCHARGE OF NEGATIVE ELECTRICITY

where i denotes the thermionic current per sq. cm., and e the charge carried by one electron. The charge e is 4.9×10^{-10} E.S. un. and is equal to the charge on one monovalent ion in solutions.

Let N denote the number of molecules in one gram molecule of any gas, and let $N\epsilon\phi = P$, so that P is the work required to enable N electrons to escape. Also, let the mean kinetic energy of an electron be equal to $\alpha\theta$, where α is a constant and θ the absolute temperature. For any gas $R\theta = \frac{3}{2}N\alpha\theta$, where R denotes the gas constant for one gram molecule. Also $q = \frac{3}{2V^2} = \frac{3m}{4\alpha\theta}$ that $\frac{2\phi\epsilon q}{m} = \frac{P}{R\theta}$.

Hence—
$$i = ne \sqrt{\frac{R\theta}{2\pi m N}} e^{-P/R\theta}$$

Now R for one gram molecule is very nearly equal to two small

calories, hence—
$$i = ne \sqrt{\frac{R\theta}{2\pi m N}} e^{-P/2\theta}$$

where P is now the energy in small calories required for escape of N electrons.

If we put $D = ne \sqrt{\frac{R}{2\pi m N}}$ this equation becomes $i = D\theta^{1/2} e^{-P/2\theta}$, which is of the same form as the equation which we have seen represents the observed thermionic currents. However, it does not follow that $D = A$ and $P = Q$, as might be thought at first sight; for P and D may not be constants. We have $D\theta^{1/2} e^{-P/2\theta} = A\theta^{1/2} e^{-Q/2\theta}$ or $P = Q + 2\theta \log D/A$, so P and D must satisfy this equation. P , therefore, must be equal to Q at the absolute zero of temperature. It will be seen in the following chapter that P does vary, and so is not equal to Q at high temperatures. D also is not equal to A .

It is important to bear in mind the distinction between P , Q and between D and A .

We can easily show that the distribution of velocities among the electrons which escape is the same as among those which enter the double layer. The number entering per sq. cm. in

second is
$$\int_0^{\infty} n(q) \frac{1}{2} q^2 dq = \frac{n}{2} \int_0^{\infty} q^2 dq$$

so that the fraction $2qve^{-v^2}dv$ have normal velocities between v and $v + dv$. The velocity of these after passing through the layer is $\sqrt{v^2 - \frac{2\phi e}{m}}$; so that the number escaping with velocities between v and $v + dv$ is

$$nv \left(\frac{q}{\pi}\right)^{\frac{1}{2}} e^{-q\left(v^2 + \frac{2\phi e}{m}\right)} dv$$

If we divide this by the total number which escape—

$$\frac{n}{2\sqrt{\pi q}} e^{-\frac{2\phi e q}{m}}$$

we get $2qve^{-v^2}dv$, the same as for those which enter the double layer.

Consider a cone of small solid angle $d\omega$ with its vertex at a small element of area ds on the surface of the hot platinum. Let the angle between the axis of the cone and the normal to ds be θ . We can easily show that the number of electrons emitted by ds which move off inside the cone is proportional to $\cos \theta$. Of the electrons emitted, the fraction whose three velocity components lie between u and $u + du$, v and $v + dv$, and w and $w + dw$ respectively, is equal to

$$\frac{2q^2 v}{\pi} e^{-V^2} du dv dw$$

where $V^2 = u^2 + v^2 + w^2$. For those inside the cone $v = V \cos \theta$ and $du dv dw = V^2 d\omega dV$, so that the fraction in the cone is

$$\frac{2q^2 \cos \theta d\omega}{\pi} \int_0^\infty V^3 e^{-V^2} dV = \frac{d\omega \cos \theta}{\pi} \quad (2)$$

Suppose we have a plane surface of hot platinum, and parallel to it a plane conductor. Let the conductor be charged negatively, so that there is a uniform electric field between the platinum and the conductor. If the difference of potential between the conductor and the platinum is ψ , then only those electrons which enter the double layer with normal velocity greater than $\sqrt{\frac{2(\phi + \psi)e}{m}}$ will have enough energy to get across to the conductor. The current to the conductor will therefore be given by

ELECTRICAL PROPERTIES OF FLAMES

the R for the electrons. The values they obtained were ranged around the value of R for gases at the temperature θ .

The agreement of the formulæ (1) and (3) with the experimental results justifies the assumption made that the distribution velocities among the electrons is that given by Maxwell's law.

In Richardson and Brown's experiment a thin flat strip of platinum heated by a current was placed close and parallel to a plane electrode, and the thermionic current from it was allowed slowly charge up another insulated electrode parallel to the first. The rise of the potential of the insulated electrode was measured with a quadrant electrometer.

In Fig. 3 the curve shows the relation between the thermionic current and the potential difference, while the straight line gives the relation between the logarithm of the current and the potential difference. From the slope of the straight line $N_e/R\theta$ can be immediately obtained, and hence R . The value of R comes out 2, instead of the theoretical value 2.

Richardson¹ has also made experiments on the distribution of the velocity components parallel to the surface of the hot platinum.

In these experiments a narrow strip of platinum about 2 cms. long was mounted in a slit cut in a plane electrode, so that the surface of the strip was flush with that of the electrode. A second plane electrode was placed parallel to the first and about 5 cm. distant from it. The second electrode also contained a slit parallel to the platinum strip, and the current carried by the electrons emitted by the platinum which entered this slit was measured. The second electrode could be moved parallel to the first in a direction perpendicular to the slits. The whole was contained in an exhausted vessel. The variation of the charge entering the slit in the second electrode as this was moved across the front of the hot strip was determined.

The slit in the movable electrode was much shorter than the hot strip, so that the strip could be regarded as of infinite length without very serious error, and the velocities parallel to the length of the strip disregarded.

It will suffice to consider the theoretical distribution in two

¹ *Phil Mag.*, December 1908.

cases, first when the potential difference between the electrodes is large, and second when it is zero.

In the first case, the initial velocity of the electrons perpendicular to the electrodes can be neglected, so that the time taken by an electron to go across to the movable electrode is $\sqrt{2dm/Xe}$, where d is the distance between the electrodes and X the electric field strength. For Xe/m is the acceleration of the electrons.

Let u denote the velocity component of an electron in a direction perpendicular to the length of the strip and parallel to the electrodes. Among n electrons emitted, the number for which u is between u and $u + du$ is given by

$$dn = n \left(\frac{q}{\pi} \right)^{\frac{1}{2}} e^{-qu^2} du$$

Let x denote the displacement of the movable slit from the position opposite to the strip, then if $u\sqrt{2dm/Xe} = x$ the electrons will go into the slit. Hence the charge entering the slit will be proportional to $e^{-qeXx^2/2dm}$. If, then, i_x is the current entering the slit, we have

$$\frac{i_x}{i_0} = e^{-qeXx^2/2dm}$$

where i_0 is the current when $x = 0$. Substituting V/d for X where V is the P.D. between the electrodes, and using the value given above for q , this becomes

$$\frac{i_x}{i_0} = e^{-NeVx^2/4Rd^3}$$

The following table is taken from Richardson's paper :—

$\pm x$ (1 = .0318 cm.)	0	1	2	3	4	5	6	7
+ i_x	1.35	1.38	1.17	.75	.51	.34	.19	.09
- i_x	1.35	1.25	1.09	.85	.47	.30	.21	.13
i_x (calculated)	1.38	1.31	1.10	.83	.56	.34	.18	.09

The values of i_x (calculated) are those given by the equation $i_x = 1.38 \times 10^{-24} x^2$. Thus, the observations agree very well with the theoretical equation. The value of R can be calculated from the results, for all the other quantities in the equation are known. In the above experiment $V = 10.6 \times 10^8$ E.M. units, $Ne = 964$ E.M. units, $\theta = 1500$ Abs., and $d = 0.534$ cm. These give $R = 2$.

small calories, which is 25 per cent. greater than the true value.

When the potential difference between the two electrodes is zero, the electrons will travel in straight lines

Equation (2) shows that the number of electrons falling on an element ds of the slit from an element of the strip is proportional to the solid angle which ds subtends at the element of the strip, multiplied by $\cos \theta$. If we take the strip to be infinitely long, it follows that the number falling on the slit is proportional to the angle subtended by the breadth of the slit at the strip and to $\cos \theta$. Thus—

$$\frac{i_1}{i_0} = \frac{d}{d^2 + x^2} \cos \theta = \left(\frac{d^2}{d^2 + x^2} \right)^{3/2}$$

In this case, also, Richardson¹ found the observed and calculated currents to agree as well as could be expected.

It appears, therefore, that the theory considered leads to results which agree well with the facts. The experiments described give striking verification of Maxwell's law of the distribution of velocities among the electrons

The formula $i = D\theta^{1/2}e^{-P/2\theta}$ can be obtained thermodynamically if we assume the emission of the negative electrons to be analogous to the evaporation of a liquid²

If p is the vapour pressure of a liquid, and L its latent heat of evaporation per gram molecular weight, then $L = (v_2 - v_1) \theta \frac{dp}{d\theta}$, where v_2 = volume of vapour and v_1 = volume of liquid. Neglecting v_1 and putting $v_2 = R\theta/p$, we get $L = \frac{R\theta^2}{p} \frac{dp}{d\theta}$. Let the internal work done in evaporating the liquid be P , so that $L = P + pv$ and

$$P + R\theta = \frac{R\theta^2}{p} \frac{dp}{d\theta}$$

hence—

$$R \log \frac{\theta_1 p_2}{\theta_2 p_1} = P \left(\frac{1}{\theta_2} - \frac{1}{\theta_1} \right)$$

Now $p = bmVN$, where m is the mass of a molecule, V the mean root of the mean square of the velocities of all the mole-

¹ *Phil. Mag.*, November 1909.

² H. A. Wilson, *Phil Trans A.* vol. 202, pp. 243-275, 1903.

cules, and N the number leaving each sq. cm. of the liquid surface per second, and b a constant. But V^2 is proportional to θ , hence we may write $p = b'N\sqrt{\theta}$, where b' is a constant. Putting this in the above equation, we get—

$$\log \frac{\theta_1^{\frac{1}{2}} N_2}{\theta_2^{\frac{1}{2}} N_1} = \frac{P}{R} \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right)$$

But $i = Ne$ and $R = 2$, so that

$$\log \frac{\theta_1^{\frac{1}{2}} i_2}{\theta_2^{\frac{1}{2}} i_1} = \frac{P}{2} \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right)$$

which is equivalent to $i = D\theta^{\frac{1}{2}} e^{-P/2\theta}$.

For pure platinum in a vacuum, or in air at low pressure, O. W. Richardson, H. A. Wilson, F. Horton, Deininger,¹ and others have all obtained values of Q differing little from 130,000. As to A , however, there is a good deal of doubt, for a small error in the currents leads to a large error in A , and traces of hydrogen or other impurities change A much more than Q . It is probable that A for pure platinum is not much less than 10^8 .

¹ *Ann der Phys* IV vol. LV. p 304, 1908.

CHAPTER III

THE DISCHARGE OF NEGATIVE ELECTRICITY BY HOT PLATINUM IN HYDROGEN AND OTHER GASES

WHEN platinum is heated in gases such as oxygen, nitrogen, helium, which have little or no action on it, the negative thermionic current is not directly affected.¹ The potential difference required to give the saturation current is increased, as should expect. If the electric field near the hot wire exceeds a certain value, proportional to the pressure of the gas, the electrons acquire sufficient energy to ionize the molecules with which they collide,² so that then the current is increased by the presence of the gas. This effect led some experimenters to suppose that the gas really increases the number of electrons emitted by the wire, but it was shown by the writer (*loc. cit*) that ionization by collisions is sufficient to account for it.

In hydrogen, however, the negative thermionic current is greatly increased, even when the hydrogen is only present in minute quantities.³

The following table gives the currents observed when successive small quantities of pure hydrogen were admitted into an apparatus like that shown in Fig. 1. The temperature of the platinum wire loop was 1350° C

Pressure of Hydrogen (p) mm. of Mercury	Thermionic Current (c) Scale Divisions	$c(10+p) - 74$
0.0006	10	2.65
0.0015	20	2.70
0.0033	40	3.01
0.0053	50	2.65
0.0080	75	2.92
0.0140	110	2.85

H. A. Wilson, *Phil. Trans. A.* vol. 202, p. 243, 1903; F. Horton, *Phil. Trans. A.* vol. 207, p. 149, 1908.

J. S. Townsend, *The Theory of Ionization of Gases by Collision.*

¹ H. A. Wilson, *Phil. Trans. A.* vol. 208, p. 247, 1908.

The values of $cp^{-7/4}$ given in the third column are nearly constant, showing that the current is proportional to $p^{7/4}$ at 1350°C . The current from a clean wire at 1350°C in a good vacuum, when all traces of hydrogen have been removed by letting in air and pumping it out several times with the wire at a high temperature, is usually not more than $1/250$ in the units used. It appears, therefore, that at a pressure of 0.014 mms. at 1350°C . the hydrogen increases the thermionic current about 25000 times.

It is very difficult to get rid of traces of hydrogen in highly exhausted tubes, so that it often happens that comparatively large currents are obtained. When the wire is heated, hydrogen may be evolved by the surrounding electrode, by the wire itself, or even by the glass. Since oxygen does not appear to affect the negative thermionic current, a simple way of getting its true value in the absence of hydrogen is to let in a little pure oxygen or air. Any hydrogen present is then burnt up at the hot wire, and the water vapour formed can be absorbed by phosphorus pentoxide. The potential difference used must not be sufficient to produce ionization of the oxygen by collisions.

When the pressure of the hydrogen is changed the resulting change in the thermionic current does not all occur immediately, but takes time to become established. The current variation lags behind that of the pressure. The same thing happens when the temperature of the wire is altered in hydrogen at constant pressure. This clearly indicates that the increase in the current produced by the hydrogen is due to the presence of hydrogen in the surface of the platinum, and that it takes time for the equilibrium between the metal and the gas to be established after any change in the conditions. The time required for the current to become constant varies considerably with the temperature and pressure. Half an hour is usually more than sufficient, even after a large change.

At constant pressure the variation of the equilibrium current with the temperature is represented approximately by the formula $i = A\theta^{1/2}e^{-Q/2\theta}$, which holds good in a vacuum. The following table contains values of A and Q found by the writer.¹

Gas	Pressure	Q.	A
Air	Small	145,000	1.14×10^8
Air	Small	131,000	6.9×10^7
H	0.0013 mm	110,000	10^6
H	0.112 mm	90,000	5×10^4
H	113.00	56,000	2×10^2

The second values in air are for a wire which had been boiled in nitric acid for one hour, and the first for one boiled in nitric acid for twenty-four hours. In both cases the wire was heated strongly while air was let in and pumped out several times. In the second case it seems likely that a minute trace of hydrogen still remained in the wire.

It will be observed that the hydrogen diminishes both Q and A . At constant pressure we have $i = A\theta^{\frac{1}{2}}e^{-Q/\theta}$, where A and Q are functions of p , and at constant temperature $i = Bp^n$, where B and n are functions of θ only.

Let i_1 and i_2 be the currents at θ_1 and θ_2 when the pressure is p . Then—

$$\frac{i_1}{i_2} = \left(\frac{\theta_1}{\theta_2}\right)^{\frac{1}{2}} e^{-\frac{Q}{2}\left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right)}$$

Now let i_1' and i_2' be the currents at θ_1 and θ_2 when the pressure is p' . Then—

$$\frac{i_1'}{i_2'} = \left(\frac{\theta_1}{\theta_2}\right)^{\frac{1}{2}} e^{-\frac{Q'}{2}\left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right)}$$

where Q' is the value of Q at p' . Also let $i_1 = B_1 p^{n_1}$, $i_1' = B_1 p'^{n_1}$, $i_2 = B_2 p^{n_2}$, and $i_2' = B_2 p'^{n_2}$. Hence—

$$\frac{i_1}{i_2} \cdot \frac{i_2'}{i_1'} = \left(\frac{p}{p'}\right)^{n_1 - n_2} = e^{\frac{1}{2}\left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right)(Q' - Q)}$$

or

$$\frac{n_1 - n_2}{\frac{1}{\theta_1} - \frac{1}{\theta_2}} = \frac{Q' - Q}{2 \log \frac{p}{p'}}$$

In this equation the right-hand side is a function of p only, and the left one of θ only. Hence both sides must be equal to a constant a say. Consequently $n = a\theta^{-1} - c$ and $Q = U - 2a \log p$, where c and U are constants. If these values are put in the

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equation $Bp^n = A\theta^c e^{-Q/2\alpha}$ we easily see that A must be equ to Kp^{-c} , where K is a constant.

If we take $\alpha = 2400$, we get the following values of $Q + 2\alpha \log p = U$.

p	Q	U
0.0013	110,000	78,000
0.112	90,000	79,500
133.0	56,000	79,500

If we take $C = 0.73$ we get the following values of $Ap^c = K$.

p	A	K
0.0013	10^6	7,800
0.112	5×10^4	10,100
133.0	2×10^3	3,600

Thus, while p is increased 10^5 times, U remains practically unchanged and K only varies by a factor of 3. A small error in the observed currents produces a large one in A , so that this quantity cannot be found very exactly. It seems, therefore, that the values found for A and Q agree well with the assumption that the current is proportional to p^n at constant temperature.

The equations $A = Kp^{-c}$ and $Q = P - 2\alpha \log p$ give

$$A = K e^{\frac{c}{2\alpha}(Q-P)} \quad \dots \dots \dots (1)$$

Putting $U = 79000$, $\alpha = 2400$, $K = 9000$, and $c = 0.73$, and calculating Q from the values found for A , the following results are obtained.—

$$Q = 6580 \log A + 19100$$

Gas	Pressure	A	Q (Calculated)	Q (Found)
Air	Small	1.14×10^6	142,000	146,000
Air	Small	7×10^7	138,000	131,000
H ₂	0.0013	10^6	110,000	110,000
H ₂	0.112	5×10^4	90,300	90,000
H ₂	133.0	2×10^3	54,000	56,000

It appears that this relation is satisfied by the values of A and Q for a wire in air, as well as by those for the wire in hydrogen.

If we put $p = 0$ in the equations $Q = P - 2\alpha \log p$ and

fore require modifying to enable them to represent all the values of A and Q . If we suppose $A = A_0/(1 + \alpha p^c)$ where α is a constant, then, when αp^c is large compared with unity, this formula will agree with $A = Kp^{-c}$ and when $p = 0$ it gives $A = A_0$. We have

$$\alpha = \frac{A_0}{K} = \frac{1.14 \times 10^8}{9 \times 10^3} = 1.27 \times 10^4$$

When $p = 0.001$, $\alpha p^c = 100$, so that even at this pressure the difference between the two formulæ is only one per cent.

Equation (1) gives $A = A_0 e^{\frac{c}{2\alpha}(Q - Q_0)}$, so that

$$Q = Q_0 - 2\alpha c^{-1} \log(1 + \alpha p^c)$$

This formula gives $Q = Q_0$ when $p = 0$, and for all measurable values of p does not differ appreciably from

$$Q = Q_0 - 2\alpha \log p - 2\alpha c^{-1} \log \alpha.$$

When $p = 1$, $Q = U$, so that this is the same as $Q = U - 2\alpha \log p$, which has been shown to agree with the values found for Q at different pressures

If we substitute the values found for A and Q in the equation $i = A\theta^{\frac{1}{2}c - Q/2\theta}$ we get

$$i = A_0(1 + \alpha p^c)^{\left(\frac{c}{2\theta} - 1\right)} \theta^{\frac{1}{2}c - Q_0/2\theta}.$$

If $p = 0$, this gives $i_0 = A_0 \theta^{\frac{1}{2}c - Q_0/2\theta}$,

so that
$$\frac{i}{i_0} = (1 + \alpha p^c)^{\left(\frac{c}{2\theta} - 1\right)}$$

which gives the ratio of the negative thermionic current in a vacuum or in air to that in hydrogen at pressure p . Also $c = 0.73$, $\alpha = 1.27 \times 10^4$, and $\alpha = 2400$.

At 900°C , in hydrogen at 26 mms. pressure, Richardson¹ found i/i_0 to be 4×10^8 . The above equation gives 2×10^9 . Since a small error in c produces a large error in i/i_0 the agreement in this case is as good as could be expected. Thus, if we take $c = 0.78$, instead of 0.73, we get $i/i_0 = 3 \times 10^8$.

At 1570°C , in hydrogen at 760 mms. pressure, G. H. Martyn² found $i/i_0 = 4.4 \times 10^4$. The formula gives 6.5×10^4 . At 1343°C ,

¹ Phil. Mag. 4 vol 907 n 1 1908

² Phil. Mag. August 1907

in hydrogen at 0.0013 mm., I found $i/i_0 = 170$. The formula gives 122

It appears, therefore, that the equation—

$$\frac{i}{i_0} = (1 + ap^c)^{\left(\frac{a}{\theta c} - 1\right)}$$

represents the values found by different observers as well as could be expected for pressures from zero to 760 mms., and for temperatures from 900° C. to 1600° C. Within these limits i/i_0 varies from unity to more than 10^8 . It seems clear, therefore, that the equations $i = Bp^n$ and $i = A\theta^{\frac{1}{2}}\varepsilon^{-Q/2\theta}$ which were assumed at the start are very approximately true. It is also clear that the thermionic current has a definite value capable of being reproduced by different observers.

The values of n given by $n = a\theta^{-1} - c$ also agree within the limits of error with those calculated directly from various observations. It is important to observe that i/i_0 diminishes rapidly with rising temperature: thus at 800° C. and one mm. pressure $i/i_0 = 3.4 \times 10^3$, while at 1800° C. it is only 2.4×10^2 .

Since the thermionic current varies continuously with the pressure of the hydrogen, it follows that the hydrogen is dissolved in the platinum. For if a definite compound were formed, then if the pressure were above its dissociation pressure, combination would be complete, and the state of the platinum would be independent of the pressure; while if the pressure were less than the dissociation pressure, all the compound would decompose.

According to the theory explained in the first chapter, the constant D in the theoretical formula $i = D\theta^{\frac{1}{2}}\varepsilon^{-T/2\theta}$ is equal to $ne\sqrt{R/2\pi Nm}$, so that it should be proportional to the number (n) of free electrons per c.c. in the platinum. We have seen that A in the experimental formula $i = A\theta^{\frac{1}{2}}\varepsilon^{-Q/2\theta}$ may be diminished by hydrogen, from 10^3 to 10^2 . But the conductivity of the platinum is very little affected by the hydrogen, so that n must really be practically unchanged. At first sight, therefore, the diminution of A appears to be incompatible with the theory.

Richardson¹ pointed out that if Q varies with the temperature, the value of A deduced from the observed currents may

¹ *Phil. Trans. A* vol 201, p 497, 1903.

differ greatly from the theoretical value $D = ne\sqrt{R/2\pi Nn}$. Thus, suppose $P = Q + \alpha\theta$. Then the equation $i = D\theta^{\frac{1}{2}}\varepsilon^{-p/2\theta}$ becomes

$$i = D\varepsilon^{-\alpha/2}\theta^{\frac{1}{2}}\varepsilon^{-Q/2\theta},$$

so that the value of A calculated from the currents is $D\varepsilon^{-\alpha/2}$ and the value of Q calculated is not equal to P

Equating the theoretical and experimental expressions for the thermionic current, we get

$$D\theta^{\frac{1}{2}}\varepsilon^{-P/2\theta} = A\theta^{\frac{1}{2}}\varepsilon^{-Q/2\theta}$$

or $P = Q + 2\theta \log D/A$ (1)

so that if P and D satisfy this equation, then the observed currents will agree with the formula $i = A\theta^{\frac{1}{2}}\varepsilon^{-Q/2\theta}$, as is found to be the case. Consequently, P and D may be any functions of θ and p which satisfy (1), and yet the formula $i = A\theta^{\frac{1}{2}}\varepsilon^{-Q/2\theta}$, in which A and Q are constants, will agree with the observed currents

According to the electron theory of metallic conduction, it is probable that n does not vary very much with the temperature. The conductivity is roughly inversely proportional to the absolute temperature for most metals. According to the electron theory the conductivity is proportional to $ne^2\lambda/mV$, where λ is the mean free path of the electrons. Now V is proportional to $\sqrt{\theta}$, so that if λ is independent of the temperature, this requires n to be inversely proportional to $\sqrt{\theta}$ to make the conductivity inversely proportional to θ . In the measurements of the thermionic currents the range of temperature is not very large usually, so that the variation of $\sqrt{\theta}$ is comparatively small. Consequently, we may suppose n to be independent of θ without serious error.

If we suppose that n and so D are independent of the temperature, then, according to the theory,

$$P = Q + 2\theta \log D/A$$

must increase uniformly with θ . According to this view, the changes in A with the pressure of the hydrogen are to be ascribed to the variation of P with the temperature, and not to any change in D . Also it follows that the number of electrons per c.c cannot be even roughly calculated from the value found for A . In order to get D and P it is necessary to make some hypothesis to explain the variation of P with the temperature.¹

¹ H. A. Wilson, *Phil. Trans. A.* vol. 208, p. 247, 1908.

To explain the energy necessary to enable an electron to escape from the platinum we supposed that an electrical double layer exists at the surface. Let this consist of an infinitely thin layer of electricity at a distance t from the platinum, having a charge σ per sq. cm. If no electrons were present the difference of potential between the layer and the platinum would be $4\pi\sigma t$, but actually electrons will be present in between the layer and the platinum, and will increase the electric force. This effect will increase as the temperature rises, so that if P is due to such a layer, it will vary with the temperature.

Let n denote the number of electrons per c.c. at a point at a distance x from the platinum. Let p denote the gas pressure due to the electrons, and ρ denote the electric volume density so that $\rho = ne$. Then when there is equilibrium we have $-dp/dx + F\rho = 0$, where F denotes the electric force inside the double layer. Now, at the layer of electricity ρ is very small, since only a minute fraction of the electrons escape, consequently at $x = t$ $F = -4\pi\sigma$ and $dF/dx = 0$

Let $p = -\beta\rho$, where β is a constant at constant temperature, so that

$$-\frac{dp}{dx} = \beta \frac{d\rho}{dx} = \frac{\beta}{4\pi} \frac{d^2F}{dx^2}$$

Hence—
$$\beta \frac{d^2F}{dx^2} + F \frac{dF}{dx} = 0,$$

which gives
$$\beta \frac{dF}{dx} + \frac{1}{2}F^2 = c.$$

When $x = t$ this becomes $c = 8\pi^2\sigma^2$,

so that
$$2\beta \frac{dF}{dx} + F^2 = 16\pi^2\sigma^2.$$

Integrating, this gives

$$\frac{F}{a} = \frac{(F_0 + a) e^{ax/\beta} - (a - F_0)}{(F_0 + a) e^{at/\beta} + (a - F_0)}$$

where $a = 4\pi\sigma$.

At $x = 0$ $\rho = \rho_0$, so that $8\pi\beta\rho_0 + F_0^2 = a^2$. Now F_0 will be nearly equal to $-a$, so that this gives approximately

$$F_0 + a = \beta\rho_0/\sigma.$$

Hence—

$$\frac{F}{4\pi\sigma} = \frac{\frac{\beta\rho_0}{8\pi\sigma^2} \varepsilon^{ax/\beta} - 1}{\frac{\beta\rho_0}{8\pi\sigma^2} \varepsilon^{ax/\beta} + 1}$$

This gives

$$V = - \int_0^x F dx = -\beta \log \left(1 + \frac{4\pi\sigma^2}{\rho_0\beta} \varepsilon^{-4\pi\sigma t/\beta} + \frac{\rho_0\beta}{16\pi\sigma^2} \varepsilon^{4\pi\sigma t/\beta} \right) - \beta \log \left(1 + \frac{4\pi\sigma^2}{\rho_0\beta} + \frac{\rho_0\beta}{16\pi\sigma^2} \right)$$

In this equation the terms—

$$\frac{\rho_0\beta}{16\pi\sigma^2} \varepsilon^{4\pi\sigma t/\beta} \quad (= 10^{-14}) \text{ and } 1$$

are quite negligible compared with $\frac{4\pi\sigma^2}{\rho_0\beta} \varepsilon^{-4\pi\sigma t/\beta}$ ($= 10^{14}$), so that we get

$$V = -\beta \log \frac{4\pi\sigma^2}{\rho_0\beta} \varepsilon^{-4\pi\sigma t/\beta} + \beta \log \left(1 + \frac{4\pi\sigma^2}{\rho_0\beta} + \frac{\rho_0\beta}{16\pi\sigma^2} \right)$$

which gives, putting $\beta = \beta_0\theta$,

$$V = 4\pi\sigma t + 2\beta_0\theta \log \left(1 + \frac{\rho_0\beta_0\theta}{8\pi\sigma^2} \right).$$

Now P , the work in calories required for N electrons to escape, is equal to NeV/J , where J is the mechanical equivalent of heat; also, since $P = Q$ when $\theta = 0$, we can put $Q = 4\pi\sigma tNe/J$ and so obtain

$$P = Q + \frac{2\beta_0\theta eN}{J} \log \left(1 + \frac{2\beta_0\rho_0\theta\pi t^2 e^2 N^2}{Q^2 J^2} \right).$$

Comparing this with $P = Q + 2\theta \log D/A$ we get

$$\log \frac{D}{A} = \frac{\beta_0 eN}{J} \log \left(1 + \frac{2\pi\rho_0\beta_0\theta t^2 e^2 N^2}{Q^2 J^2} \right).$$

Since $p = -\rho\beta_0\theta = -ne\beta_0\theta$ we see that $-\beta_0 eN$ is equal to the gas constant, hence $\beta_0 eN/J = -2$ calories. Hence—

$$t^2 = \frac{Q^2\beta_0}{8\pi\rho_0\theta} \left(\left(\frac{A}{D} \right)^{\frac{1}{2}} - 1 \right).$$

If we take two values of Q , Q_1 and Q_2 , and the corresponding values A_1 and A_2 , we get

$$D = \left\{ \frac{Q_1^2 A_1^{\frac{1}{2}} - Q_2^2 A_2^{\frac{1}{2}}}{Q_1^2 - Q_2^2} \right\}^2$$

This equation, with the values found for A and Q, give $D = 3.7 \times 10^8$.

Having found D we can use it to calculate the value of ne . We have $D = ne\sqrt{\frac{R}{2\pi Nm}}$. Here $R = 84 \times 10^7$ ergs, $Ne = 9644$ E M units, and $e/m = 1.7 \times 10^7$ in E M units as for cathode ray. Putting in these values and $D = 3.7 \times 10^8$, we get $ne = 2.4 \times 10^{10}$ coulombs, or 7.2×10^{12} E S units. Since e is equal to 4.9×10^{-10} E.S. units, this gives $n = 1.5 \times 10^{23}$ free electrons in one c.c. of platinum.

The number of atoms of platinum in one c.c. is 6×10^{23} , so that there is one free electron for every four atoms.

The expression for t then gives the following values:—

Q	A	t
145,000	1.14×10^8	9.6×10^{-8} cm.
131,000	6.9×10^7	9.9 "
110,000	10^8	10.7 "
90,000	5×10^4	9.0 "
56,000	2×10^2	5.6 "

The five values of t agree as well as could be expected.

It is interesting to apply the formula for t to platinum polarised with hydrogen in dilute sulphuric acid. The potential fall in this case is about 0.9 volt, which corresponds to a value of Q about 2.1×10^4 . If, then, we suppose A/D to be small

which is the case in hydrogen at high pressures, we get $t^2 = \frac{Q^2 \beta}{8\pi\rho_1}$

which gives at $\theta = 300$, $t = 4.8 \times 10^{-8}$. The thickness of the double layer in this case has been estimated by several observers from the polarisation capacity, and found to be about 2×10^{-8} cm.

Thus the theory proposed leads to probable values of the thickness of the double layer and of the number of free electrons per c.c. in the platinum, so that it seems adequate to explain the facts.

Substituting the values found for A, Q and D in the formula $P = Q + 2\theta \log D/A$, we get the following values of P:—

Gas	Pressure	P
Air	—	145,000 + 2 35 θ
H ₂	0 0013	110,000 + 11 83 θ
H ₂	0 112	90,000 + 17 82 θ
H ₂	133 0	56,000 + 28 86 θ

Thus, in air P only varies very slowly with the temperature

It appears, therefore, that the thickness t of the double layer on the platinum is unchanged by the hydrogen, which, however, diminishes the fall of potential across it. This effect may be due to positively charged hydrogen atoms in the double layer, but the precise way in which the hydrogen acts is unknown.

In some experiments Richardson¹ found that the leak from a hot platinum wire in hydrogen was independent of the pressure, even when this was reduced to a very small value. The writer² found that this is always the case after a wire has been heated in hydrogen at a comparatively high pressure for some time. After this treatment the properties of the wire are completely changed.

The wire, then, gives a large thermionic current practically independent of the pressure of the hydrogen, from 760 mms down to less than 0 001 mm.

The following table gives the currents observed from a wire treated in this way, at a pressure of 0 003 mm. :—

Temperature	Amperes per sq cm
1578° C	9 51 $\times 10^{-5}$
1613° C.	19 26 „
1648° C	38 7 „
1683° C	72 3 „

These numbers give $A = 1 67 \times 10^{10}$, and $Q = 135300$. The value of Q is thus nearly the same as for a wire in air, but A is 100 times larger.

If the wire is heated in air or oxygen the large thermionic current immediately disappears. It can also be made to disappear

¹ *Phil. Trans. A* vol. 207, p. 1, 1906.

² *Phil. Trans. A* vol. 208, p. 247, 1908.

by heating above 1700°C . in a very high vacuum. These facts make it very probable that the hydrogen combines with the wire forming a very stable compound. This compound must have a very small dissociation pressure. It must also be formed very slowly, unless the pressure of the hydrogen is high.

After the wire has been heated in oxygen it gives the same thermionic currents as an ordinary wire in which the compound has never been formed. However, a permanent effect seems to remain, for the time lag of the current after changes of pressure seems much greater than before.

Richardson found that increasing the potential difference from 19 volts to 286 volts caused the negative leak in hydrogen at 1.77 mms, at 1084°C to diminish gradually from 147×10^{-8} to 26×10^{-8} ampere. This effect, he suggested, may be due to the bombardment of the wire by the positive ions produced by ionisation by collisions due to the high potential. This bombardment may remove the hydrogen atoms in the double layer, and so make the negative current correspond with that due to hydrogen at lower pressure.

The writer found that a wire in hydrogen giving a negative current which was slowly increasing with the time, gave less current at high temperatures than at low. The current was saturated and rose when the temperature was diminished.

These peculiar effects seem to take place only when the wire is not in equilibrium with the hydrogen. Further investigation is required to find out their cause.

Other substances besides hydrogen have been found to increase the negative thermionic current. Thus the writer noticed a great increase due to phosphorus pentoxide¹. A systematic examination of the effects of a large number of different substances might lead to interesting results.

¹ *Phil. Trans* vol. 202, p 243

CHAPTER IV

THE DISCHARGE OF NEGATIVE ELECTRICITY BY VARIOUS SUBSTANCES

O. W. RICHARDSON¹ investigated the negative thermionic current from carbon and sodium, as well as from platinum. Both these substances gave very large currents. Sir J. J. Thomson² found the current from sodium to be greatly increased by the presence of hydrogen, so that it could be observed even at ordinary temperatures

Wehnelt³ discovered that the oxides of the alkaline earths emit a copious supply of negative electrons when heated in a vacuum. Owen⁴ measured the negative thermionic current from a Nernst lamp filament. In all these cases the formula $i = A\theta^{3/2}e^{-Q/2\theta}$ was found to represent the variation of the current with the temperature

The following table gives the values found for Q and A. Q is expressed in calories per gram molecule of electrons, and A so as to give the current in amperes per sq. cm

Substance.	Q	A
Carbon	19.6×10^4	10^{15}
Sodium	63 "	10^8
Baryta	9 "	7×10^7
Lime	8.6 "	5×10^7
Nernst filament	9.2 "	7×10^4

Owen (*loc. cit.*) examined the effect of a transverse magnetic field on the negative thermionic current, and found that a part of it was carried by heavy ions not easily deflected by the field. With platinum at 1300° C, 95 per cent of the current could be deflected by a small field, and therefore was carried by electrons.

¹ *Phil. Trans. A.* vol. 201, p. 516, 1903. In these early experiments traces of hydrogen or other impurities were probably present and caused a very great increase in the thermionic currents. See Pring and Parker, *Phil. Mag.*, Jan. 1912.

² *Conduction of Electricity through Gases*, p. 203.

³ *Ann. d. Phys.* (4) vol. xiv. p. 425, 1904.

⁴ *Proc. Camb. Phil. Soc.* vol. xii. p. 493, 1904. *Phil. Mag.* (6) 8, 230, 1904.

With new wires the percentage of heavy ions was greater than with wires which had been heated for some time.

Felix Jentzsch¹ measured the negative thermionic current from a number of metallic oxides in a vacuum. He found the following values of Q and A . The constant A gives the current per sq cm in electrostatic units.

Substances	Q	A
BaO	83.2×10^3	1.41×10^{16}
SrO	89.8 "	152 "
CaO	80.6 "	129 "
MgO	79.0 "	1×10^{10}
BeO	47.8 "	0.31 "
Y_2O_3	72.6 "	5590 "
La_2O_3	75.8 "	207 "
Al_2O_3	74.6 "	2 "
ZrO_2	73.2 "	1970 "
ThO_2	71.2 "	10.5 "
CeO_2	74.2 "	586 "
ZnO	70.2 "	0.092 "
Fe_2O_3	93.8 "	1076 "
NiO	102.4 "	8370 "
CoO	99.4 "	1595 "
CdO	60.4 "	0.11 "
CuO	45.0 "	0.001 "

It will be observed that Q does not vary very much, whereas A varies very greatly.

Jentzsch pointed out that the possible error in Q was two or three per cent., while that in A was as much as 500 per cent. Consequently, it is very difficult to get more than the order of magnitude of A .

For lanthanum oxide he gives the following table.—

Absolute Temperature.	Current (Calculated)	Current (Found)	Percentage difference
1355	13.3	12.2	8
1405	36.7	35.5	3
1450	86.2	82.4	4
1470	124	132	6
1510	249	256	3
1570	662	692	4
1625	1525	1515	1
1680	3325	3065	8
1720	5700	7160	26

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The calculated currents are those given by the equation—

$$i = 5.16 \times 10^{11} \theta_E^{-75800/2\theta}$$

Jentzsch found the currents in all cases to obey the same law

The copious emission of negative electrons by lime can be shown very clearly by means of a vacuum tube fitted with a "Wehnelt cathode." This consists of a strip of platinum foil which can be heated to incandescence by passing a current through it. On the foil is a small patch of lime, obtained by putting a drop of dilute calcium nitrate solution on it and then heating. The tube is provided with another electrode to serve as anode. If a moderate P.D.—say 200 volts—is maintained between the anode and cathode, then on heating the cathode, a narrow stream of cathode rays is emitted by the patch of lime. If the pressure is not too low, the path of this stream through the tube is visible as it emits a faint blue light. The deflection of the stream by magnetic and electric fields can be easily demonstrated owing to the low P.D., so that such a tube is very useful for showing the properties of cathode rays.

Sir J. J. Thomson found that a good way of making the patch of lime is to put a very small bit of sealing-wax on the foil and then heat it. The wax contains lime, or baryta, and gives a firmly adherent patch.

Hydrogen increases the current from lime in the same way as from platinum. Thus, G. H. Martyn¹ calculated the following negative thermionic currents at 1600° C. from observations at different temperatures —

Platinum in air	—	5×10^{-7} ampere
Lime in air		5×10^{-2} „
Platinum in hydrogen		10^{-1} „
Lime in hydrogen		10^8 „

F. Horton² gives the following values of the constants Q and A found in helium at a few mms pressure.—

Platinum	. 1.22×10^5	16×10^0
Calcium .	. 7.29×10^4	17×10^4
Lime .	. 9.58×10^4	64×10^{11}

¹ *Phil. Mag.*, August 1907.

² *Phil. Trans. A* vol. 207, p. 140, 1909.

He observed that the current from lime is greatly increased by hydrogen.

The conductivity of metallic oxides, like lime, is small at low temperatures, but increases rapidly with the temperature.

The variation of the conductivity (σ) with the temperature¹ is given at any rate roughly by the formula $\sigma = K\epsilon^{-S/2\theta}$, where K and S are constants. Hence, we have approximately $D = B\epsilon^{-S/2\theta}$, so that $\epsilon = B\theta^{2/S} \cdot (P + S)^{2/S}$.

It follows from this that the value of Q calculated from the currents observed at different temperatures with metallic oxides is not P but $P + S$. Also, the value found for A is equal to $B = D\epsilon^{-S/2\theta}$. Thus, if n for metallic oxides is calculated from the values found for A , as was done by several observers, it must be wrong by the factor $\epsilon^{-S/2\theta}$, which usually amounts to many thousands.²

O. W. Richardson³ pointed out that the escape of negative electrons from hot bodies should be accompanied by an absorption of heat, just as in the analogous case of the evaporation of a liquid.

The calculation given at the end of Chap. I shows that the latent heat of emission of one gram molecule of electrons is $P + R\theta$, so that the determination of this latent heat affords a method of finding P not Q . Wehnelt and Jentzsch⁴ found that the current required to keep a platinum wire coated with lime hot was greater when it was charged negatively and emitting electrons than when it was charged positively so that the electrons were prevented from escaping. From the difference between the two currents the heat rendered latent was calculated, and was compared with the theoretical amount calculated from the thermionic current and the known value of Q for lime. The observed values, however, came out several times larger than those calculated. This is especially remarkable, because the value of P must be considerably smaller than the value of Q calculated from the thermionic currents, which, as we have seen, is equal to $P + S$.

¹ F. Horton, *Phil. Mag.*, April 1906

² H. A. Wilson, *Phil. Trans. A* vol 208, p. 247, 1908.

³ *Phil. Trans. A* vol 201, p 497, 1903.

⁴ *Ann. d. Phys* vol, 28, p 537, 1909

The reason for the discrepancy is not known. Possibly it is due to unavoidable errors in measuring such small quantities. Further experiments are desirable to clear up this question.

When the electrons emitted by a hot body are absorbed by a cold electrode we should expect an evolution of heat. This effect was observed by Richardson and Cooke¹. The cold electrode used by them was a strip of platinum, and the heat developed was estimated from its change of resistance due to the rise in temperature. They measured the heat developed in the platinum strip when it had been treated with nitric acid to remove hydrogen, also when it had been saturated with hydrogen. In the first case the mean value of P deduced from the observed heating effect was 128,000, and in the second case 105,000. The temperature of the cold electrode was probably not more than 500° Abs. so that to compare the values found for P with those calculated from the thermionic currents we require the values at 500° Abs.

The value of P for pure platinum given by the expression $P = 145000 + 2.35\theta$ at 500° Abs. is 146,000, which does not differ much from 128,000. Also, 146,000 is rather higher than the value of Q found by most observers, which is about 130,000, which would make P at 500° Abs. 131,000. For platinum in hydrogen at 0.112 mm. $P = 56000 + 28.86\theta$. This makes P at 500° Abs. equal to 70,000, which is rather less than Richardson and Cooke's value of 105,000. For hydrogen at 0.112 mm. P at 500° Abs. comes to 99,000 and so agrees very well with 105,000. It seems likely that though the platinum strip was saturated with hydrogen, before putting it in the apparatus most of the hydrogen must have escaped when the pressure was reduced to a small value. Consequently, the amount remaining in the platinum may very likely have been about that corresponding to a pressure of 0.112 mm.

It will be observed that since Q is only equal to P at 0° A. it is not correct to compare the value of P deduced from the heat effect directly with Q .

It is clear that Richardson and Cooke's experiments are in excellent agreement with the theory, which thus receives interesting confirmation.

¹ *Phil. Mag.*, July 1910.

CHAPTER V

THE DISCHARGE OF POSITIVE ELECTRICITY BY HOT BODIES.

A POSITIVE charge escapes from hot bodies in air at a rate which increases rapidly as the temperature rises

The negative thermionic current is very little affected by the presence of air, and is much smaller than the positive current unless the pressure is very low or the temperature very high. The variation of the positive thermionic current from hot platinum in air at atmospheric pressure, with the temperature, was investigated by the writer in 1901¹

The apparatus used consisted of a platinum tube 0.75 cm in diameter, which was heated in a gas furnace. Along the axis of this tube a platinum electrode 12 cms long and 0.3 cm in diameter was supported, and the current between the electrode and tube through the air was measured. A constant current of air could be passed through the tube during the measurements. The temperatures of the tube and electrode were measured by means of thermo-couples. Fig 4 shows the relation between the current and potential difference observed with this apparatus at 1080° C. without any current of air through the tube

When the inside electrode was positively charged the current was nearly saturated with 200 volts, but when the tube was positive it continued to increase up to 800 volts. When the inside electrode is positive, the ions start from it and move across to the tube, so that they start in the strong electric field close to the electrode, whereas when the current is reversed they start in the weaker field at the tube. Also, owing to the greater area of the surface of the tube, the current from it is larger and so more difficult to saturate. In this experiment with no air current the electrode was colder than the tube, which also helps to explain the larger current from the tube.

The potential difference, about 1000° C, could not be raised much above 800 volts without an arc forming between the elec-

¹ *Phil. Trans. A.* vol 197, pp 415-441, 1901

trodes. Thus the P.D required to produce saturation is not very much less than that required to spark through the gas. It was found that on heating the tube and putting on the P.D. a large current was obtained at first, which rapidly fell off and settled down to a nearly constant value in one or two minutes. After

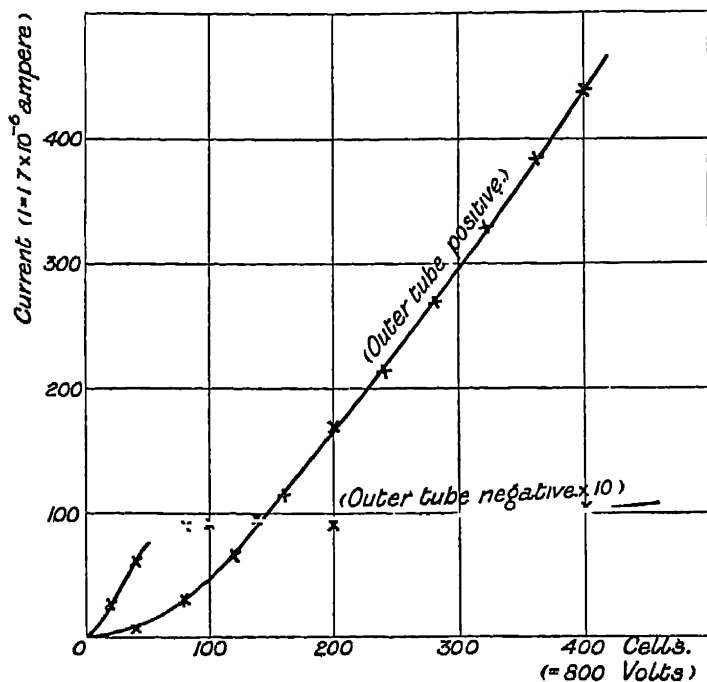


FIG. 4.

standing cold for some hours this initial large current could always be obtained. The initial current was often ten times the steady current

The steady current was found to diminish gradually from day to day. The following numbers illustrate this effect.—

Date	Temperature 900° C	Temperature 1100° C.
July 6	40×10^{-6} ampere	400×10^{-6} ampere
„ 10	11 „	140 „
„ 30	0.7 „	8 „

Fig. 5 shows the variation of the current with the temperature, using 240 volts with the inside electrode positive, so that the current was saturated. Fig. 6 shows the same thing with 40 volts, for which the current was nearly proportional to the voltage. In these experiments a rapid current of air was passed through the tube. This kept the inside tube hot, and also served to blow out

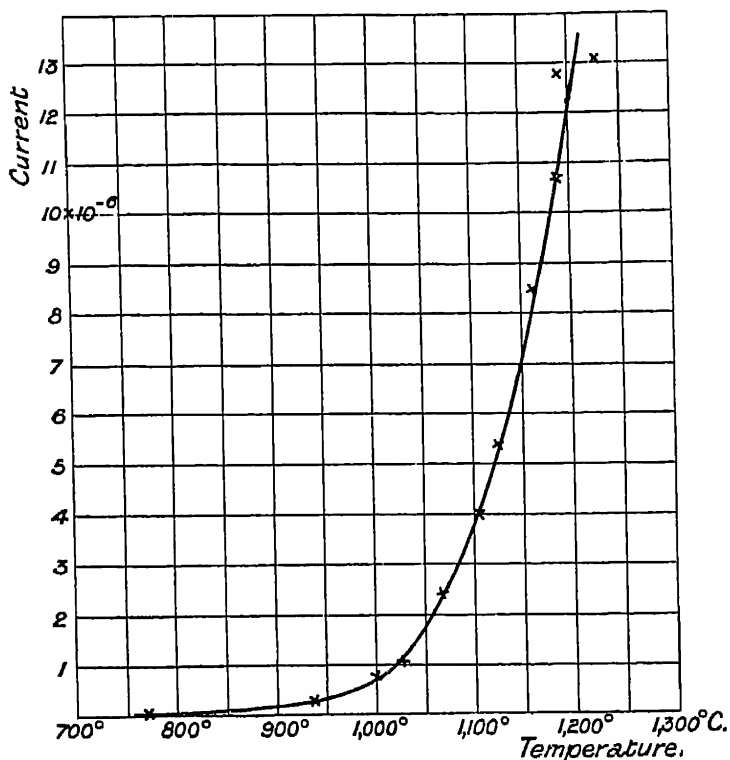


FIG 5.

the platinum dust which is emitted at high temperatures. If this dust is allowed to accumulate in the air near the platinum, the ions get stuck to it, which makes it more difficult to saturate the current. In a good vacuum there is practically no permanent positive thermionic current from hot platinum, so that we may

conclude that the steady current obtained is due to the presence of the air. The fact that the positive current is very large compared with the negative current, unless the temperature is very high, shows that the ions are formed at the surface of the platinum.

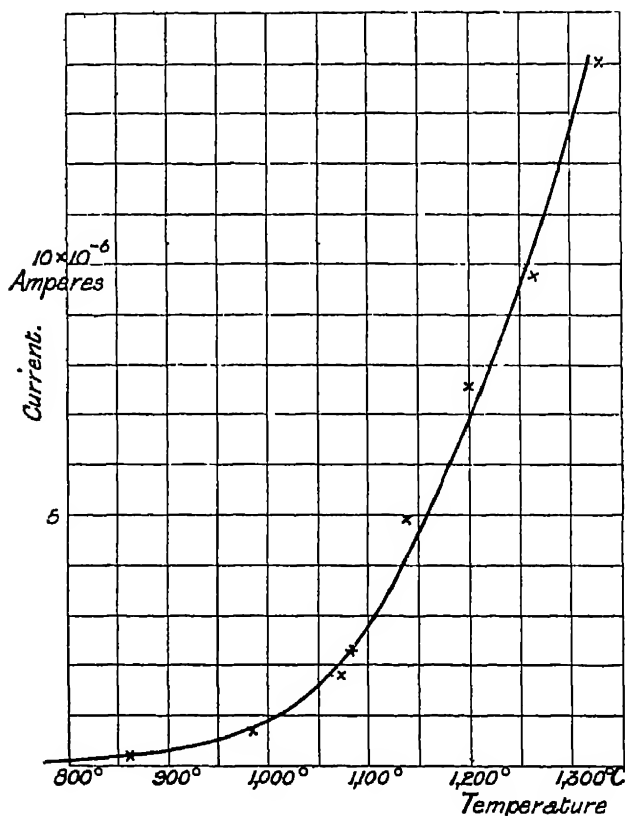


FIG. 6

The precise way in which the positive ions are formed is unknown, but if we regard the emission of positive ions as analogous to evaporation, then the calculation given at the end of Chap I can be applied, so that we should expect the saturation current carried by the positive ions to be given by the equation $i = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, where A is a constant and Q the apparent energy

rendered latent by the production of one gram molecule of ions. This equation represents the variation of the current due to 240 volts with the temperature shown in Fig. 5 fairly well if Q is taken equal to 50,000. The variation of the current due to 40 volts with the temperature shown in Fig. 6 gives values of Q which diminish as the temperature rises from 36,000 at 975°C to 25,000 at 1300°C .

The heat rendered latent by the production of ions at the surface of hot platinum was first calculated from the variation of the thermionic current in air with the temperature by the writer in 1901 (*loc cit*). It was then supposed that the air molecules dissociated into positive and negative ions at the surface of the platinum, and that there was an equilibrium between the ions and undissociated molecules. On this supposition the formula $i = A\theta^{1/2}e^{-Q/4\theta}$, where i is the current due to a small P.D., was deduced by the application of the thermodynamical theory of chemical equilibrium. The current due to a small P.D. was taken to be proportional to the concentration of the ions at the surface of the platinum. With this formula the currents in Fig. 6 give values of Q ranging from 71,000 at 975°C . to 49,000 at $1,300^{\circ}\text{C}$. It is clear now that the theory just mentioned is inadequate, because according to it we should expect the air to produce a negative thermionic current equal to the positive one, which is not found to be the case. The analogy with evaporation enables the formula $i = D\theta^{1/2}e^{-P/2\theta}$ to be deduced without making any supposition as to the precise way in which the ions are produced, but this formula is only applicable to the saturation currents.

Various suppositions can be made to explain the formation of the positive ions. We may suppose that the air molecules lose a negative electron to the hot platinum when they collide with it with a normal velocity greater than a definite value. In this way the formula $i = D\theta^{1/2}e^{-P/2\theta}$ can easily be obtained as for the negative electrons escaping from the platinum.

Just as in the case of the negative electrons, the values of A and Q calculated from the observed currents are not necessarily equal to the values of D and P . According to the supposition just mentioned D ought to be equal to $ne \cdot \sqrt{R/2\pi mn}$, where n is now

the number of molecules in one c.c. of the air, and m the mass of an air molecule

Another view which may be taken is that there is a layer of positively charged atoms, or molecules, of the gas on the surface of the platinum, held in position by the attraction due to their charges. These atoms, of course, tend to acquire the amount of kinetic energy corresponding to the temperature, and when one gets more than a certain amount we may suppose it escapes. According to this view we should expect the negative thermionic current to be increased by the presence of the gas, which is not the case, except with hydrogen

Another view, proposed by O. W. Richardson, is that the gas molecules dissociate to some extent into atoms which combine with the platinum. The compound formed dissociates into platinum and positively charged atoms of the gas. The pressure of the atoms, on this view, is proportional to the square root of the pressure of the undissociated gas. On this view, at low pressures the current should be nearly proportional to the square root of the pressure, and, at high pressures, nearly independent of the pressure, because then the combination between the platinum and oxygen is complete. If the dissociation into atoms were complete the current would be proportional to the pressure at low pressures.

It will be convenient now to consider the relation between the current and the potential difference between the electrodes

In the case of two concentric cylinders, the electric force F is given by the equation—

$$\frac{d}{dr} (Fr) = 4\pi q r$$

here q is the density of the electrification in the gas. The current c is equal to $2\pi r F q k$, where k is the velocity of the ions in e.u. Hence—

$$\frac{d}{dr} (Fr)^2 = \frac{4cr}{k}$$

that
$$(F_2 r_2)^2 - (F_1 r_1)^2 = \frac{2c}{k} (r_2^2 - r_1^2)$$

where F_2 is the field at radius r_2 and F_1 that at r_1 .

This equation shows that the electric field will not be

appreciably changed by the ions so long as $\frac{2c}{k}(r_2^2 - r_1^2)$ is small compared with $F r$.

If the field is only slightly altered by the ions we may write—

$$F r = F_1 r_1 + \delta(F r)$$

where $\delta(F r)$ is a small quantity. Hence—

$$\delta(F r) = 2\pi\rho_1(r_2^2 - r_1^2) = r\delta F$$

where ρ_1 is the density of electrification at r_1

If δV denotes the change in the P.D. due to the ions, we have, when the inside electrode is positive,

$$\delta V = \int_{r_1}^{r_2} \delta F dr = \pi\rho_1(r_2^2 - r_1^2 - 2r_1^2 \log \frac{r_2}{r_1})$$

taking r_2 to be the radius of the outer tube and r_1 that of the inner. Hence—

$$V = \frac{c}{2\pi\rho_1 k} \log \frac{r_2}{r_1} + \pi\rho_1(r_2^2 - r_1^2 - 2r_1^2 \log \frac{r_2}{r_1}).$$

In the same way, when the outside tube is positive,

$$V = \frac{c}{2\pi\rho_2 k} \log \frac{r_2}{r_1} + \pi\rho_2(2r_2^2 \log \frac{r_2}{r_1} - r_2^2 + r_1^2)$$

Putting in $r_2 = 0.375$ and $r_1 = 0.15$ cm., this becomes

$$V = \frac{0.146c}{\rho_2 k} + 0.436\rho_2$$

The curve with the outside tube positive, shown in Fig. 4, can be represented very well from 200 to 800 volts by an equation of the form $V = A c + B$, where A and B are constants. From this curve we get $B = 0.436\rho_2 = 0.5$ E.S. units, so that

$$\rho_2 = 1.15 \text{ E.S. units.}$$

Also, since $\frac{dV}{dc} = A = \frac{0.146}{k\rho_2}$ and $\frac{dV}{dc} = 10^{-5}$ in the straight part of the curve, we get

$$k = 13 \times 10^4 \text{ in E.S. units}$$

or $k = 43$ cms per sec. per volt per cm.

The curve with the inside electrode positive can also be represented by $V = A c + B$ between 20 and 100 volts, but B is too small to be estimated accurately

The current at the inside electrode when it is positive is equal to $2\pi r_1 \rho_1 k F_1$. The relation between F and the current density

was given by Sir J. J. Thomson ¹ If there are n ions per c.c. close to the electrode, the number striking it per sec per sq cm. is $nV/\sqrt{6\pi}$, where V is the velocity of agitation of the ions, according to the kinetic theory of gases. If we suppose that when an ion strikes the platinum it gives up its charge, then we have

$$I - \frac{neV}{\sqrt{6\pi}} = i$$

where I denotes the saturation current per sq cm. Also, $i = kqF$ and $k = 1.4e\lambda/mV$, so that

$$i = \frac{IF}{F + \frac{mV^2}{1.4e\lambda\sqrt{6\pi}}}$$

$\frac{mV^2}{\lambda}$ is independent of the temperature, and λ for a molecule of nitrogen at 0° C. and 760 mms is 9.5×10^{-8} cm. Also $\frac{mV^2}{ne} = \frac{3p}{ne}$, where p is the pressure of a gas containing n molecules per c.c. For a gas at atmospheric pressure, $p = 1.01 \times 10^9$, and $ne = 2.6 \times 10^{10}$, so that $\frac{mV^2}{1.4e\lambda\sqrt{6\pi}} = 2$ E.S. units. Hence

$i = \frac{IF}{F + 2}$, and since $i = e_1 k F_1$ we get $e = \frac{I - i}{2k}$. If s denotes the saturation current per cm., then $s = 2\pi r_1 I$, also $c = 2\pi r_1 i$ and $k = 1.3 \times 10^4$. Substituting these values in the expression found for V and the values of r_1 and r_2 we obtain—

$$V = \frac{0.275c}{s - c} + (s - c)10^{-5}$$

which gives V in E.S. units. The saturation-current per cm. for the curve in Fig. 4 is 5.6×10^4 E.S. units. So that for this curve—

$$V = 0.275 \frac{c}{s - c} + \left(1 - \frac{c}{s}\right) \times 0.056.$$

The following table gives values of V calculated by this equation, and also the observed values of c/s taken off the curve —

¹ *Conduction of Electricity through Gases*, p. 208, 1906.

i/I	V in volts (Calculated)	i/I (Found)
0.1	24.3	0.12
0.2	34.2	0.22
0.3	47.1	0.30
0.4	65.1	0.40
0.5	91	0.63
0.6	131	0.68
0.7	197	0.82
0.8	333	0.86
0.9	744	0.9

Owing to the small scale of Fig 4, the values of i/I could not be read off very exactly, so that the agreement between column one and column three is as good as could be expected, and provides an interesting confirmation of Sir J. J. Thomson's theory of the relation between the current and the electric force. It is plain that the value of k deduced from the currents with the outer electrode positive is consistent with the currents with the inside electrode positive.

Since $\frac{i}{I} = \frac{F}{F+2}$ the value of F required to make i 90 per cent. of I is 18 E.S. units, or 5400 volts per cm. The value of F required to spark through air at 1000° C. is probably about 6500 volts. It was found that the potential difference could not be increased much above 800 volts without an arc forming, which agrees with this estimate. Thus, to completely saturate the current was impossible, although the electrodes were only two or three mms. apart, because the necessary field is greater than that required to spark through the gas. Nevertheless, the current was 75 per cent. of the saturation current with only 200 volts, which is only one-quarter of the P.D. required to spark.

According to the equation $i = \frac{IF}{F + \frac{mV^2}{1.4e\lambda\sqrt{6\pi}}}$ the value of i/I is independent of the temperature, so that we should expect the variation of the current due to a small electric force with the temperature to be the same as for the saturation currents. Provided that the electric field is not appreciably

disturbed by the ions, we should, therefore, expect the current due to a small P.D. to be proportional to the saturation current.

The current due to 40 volts increased less rapidly with the temperature than the current due to 240 volts, especially at the higher temperatures. This is probably due to the disturbance of the electric field by the ions, which, although small at 1000°C ., increases rapidly with the temperature.

The formula $k = \frac{1.4el}{mV}$ gives $k = 65$ cms per sec. for one volt per cm for a nitrogen molecule in air at atmospheric pressure at 1000°C . This agrees as well as could be expected with the value of k found above. That slow ions were not formed by the ions sticking to platinum dust from the electrodes, was due to the dust being blown out by the air current, and to the tube having been heated for long periods before the measurements described were made.

Rutherford¹ measured the thermionic current from a sheet of platinum, heated by passing a current through it, to a parallel electrode in air at atmospheric pressure. He found the positive current diminished at high temperatures, and showed that this was due to the presence of slowly moving ions which were formed in increasing numbers as the temperature rose. He determined the velocity of the ions, and found it fell off with the distance from the hot plate. At several cms. distance it was about 1.9 cms. per sec for one volt per cm. This is not far from the velocity of the ions produced in air by Röntgen rays, which are probably single molecules of oxygen or nitrogen. The very slow ions which were present at the higher temperatures are, no doubt, formed by gas ions sticking to platinum dust. Near the hot plate the ions had much larger velocities than 1.9

If X denotes the electric force in the air between the hot platinum sheet and the parallel electrodes, then $\frac{dX}{dx} = 4\pi q$, where x is the distance from the sheet and q the density of electrification in the air. The current per sq. cm. (i) is equal to kqX , so that

$$\frac{dX}{dx} = \frac{4\pi i}{kX}$$

¹ *Physical Review*, vol. xiii, p. 321, 1901.

If we assume that k is independent of x and the same for all the ions, we get—

$$X^2 = \frac{8\pi i}{k} x + c$$

If l is the distance between the plate and electrode, and V the potential difference, then

$$V = \int_0^l X dx = \frac{k}{12\pi i} \left[\left(\frac{8\pi i l}{k} + c \right)^{3/2} - c^{3/2} \right]$$

When $x = 0$, we have $X_0 = \sqrt{c}$. When the current is small compared with the saturation current we may take it to be proportional to X_0 , so that $i = \beta X_0$, where β is a constant. Hence

$$V = \frac{k}{12\pi i} \left[\left(\frac{8\pi i l}{k} + \frac{i^2}{\beta^2} \right)^{3/2} - \frac{i^3}{\beta^3} \right] \quad \dots \quad (1)$$

When i is so small that i^2/β^2 and i^3/β^3 can be neglected, this gives approximately

$$V = \frac{k}{12\pi i} \left(\frac{8\pi i l}{k} \right)^{3/2} = \left(\frac{8\pi i}{k} \right)^{1/2} \frac{l^{3/2}}{3}$$

so that the current is proportional to V^2 and inversely proportional to l^3 .

Rutherford found that this equation represented his experimental results fairly well when l was not less than two or three cms, so that his currents were extremely small compared with the saturation currents.

When l is small, and i not too small, the equation (1) reduces to

$$V = \frac{l}{\beta} i + \frac{2\pi l^2 \beta}{k}$$

which is of the same form as we found for cylindrical electrodes when the electric field was not much affected by the ions. This equation obviously affords a simple method of finding k .

According to the equation $\frac{i}{I} = \frac{F}{F + 2}$, which we have seen represents the variation of the current with the electric force at the surface of the platinum, F must be equal to 6 E.S. units for i to be 75 per cent. of I .

To calculate the P.D. required to give about 75 per cent. of the saturation current, therefore, we may put $X_0 = \sqrt{c} = 6$; so that

$$V = \frac{k}{12\pi n} \left[\left(\frac{8\pi n l}{k} + 36 \right)^{3/2} - 216 \right]$$

If $i = 10^{-6}$ ampere, or 3000 E.S. units, $l = 5$ cms., $k = 3 \times 10^4$
this gives

$$V = 14700 \text{ volts.}$$

If $l = 0.2$ cm, we get

$$V = 336 \text{ volts}$$

In this case the average electric force $\frac{336}{300 \times 0.2} = 5.6$ ES
units, is nearly equal to X_0 , so that the electric field is practically
unaffected by the presence of the ions.

It is only when i is a small fraction of the saturation current
that the electric field is appreciably disturbed by the charge in
the gas.

It has been suggested that in my experiments the current
was always very far from saturation, so that the variation of the
current with the temperature was due to the variation of the
velocity of the ions, and not to the variation of the ionization.
That this was not the case is obvious from the fact that the
current was nearly saturated with 200 volts, and was proportional
to the P D up to about 100 volts. Also the value of Q calculated
from the saturation currents agrees with the result obtained by
W. Richardson with entirely different apparatus.

In Rutherford's experiments the variation of the current
with temperature was largely due to the variation of the velocity
of the ions, and was entirely different from the variation with
temperature in my experiments.

The initial large positive thermionic current mentioned above
is found by O. W. Richardson¹ to occur with a new platinum
wire in a vacuum, and to be proportional to $e^{-\alpha t}$, where t denotes
the time, and α is a constant. The value of α depends on the
temperature and other conditions. This suggests that this initial
current is due to the presence of some substance which disappears
at a rate proportional to the amount of it present. It disappears
almost completely after heating a new platinum wire for a short
time in a vacuum, but it can be made to reappear by allowing the

¹ *Phil Mag*, July 1903

platinum to be exposed to the air in a room. Richardson¹ found it reappeared if the wire was exposed to a luminous discharge or heated in any of the commoner gases

W. Wilson² found that heating the platinum in the presence of water, or dipping it in water, caused it to afterwards give a large positive current when heated in air at atmospheric pressure. He also found that the decay of the initial positive current only goes on while the current is flowing and not while the hot platinum is surrounded by an insulated electrode

Sir J. J. Thomson³ measured e/m for the positive ions from hot platinum in air at a low pressure.

A strip of platinum foil was arranged parallel to an insulated electrode, and 3 mms from it. The strip could be heated by an alternating current and raised to any desired potential. The electrode and strip were contained in an exhausted tube containing air at a low pressure. A magnetic field could be applied parallel to the surfaces of the strip and electrode and the current carried by the positive ions from the strip to the electrode was measured. It was found that a magnetic field of strength 19,000 completely stopped the current with a potential difference of 3 or 4 volts, but only diminished it by 75 per cent with 10 volts. The effect of the magnetic field was not appreciable with a potential difference above 120 volts.

If x is the distance of an ion from the hot strip, X the electric force parallel to x , and H the magnetic force parallel to the axis of z , then

$$m \frac{d^2x}{dt^2} = Xc + He \frac{dy}{dt} \quad . \quad . \quad . \quad (1)$$

$$m \frac{d^2y}{dt^2} = -He \frac{dx}{dt} \quad . \quad . \quad . \quad . \quad (2)$$

or

$$m \frac{d^2y}{dt^2} = -Hcx$$

since $\frac{dy}{dt} = 0$ when $x = 0$, hence, from (1)—

$$m \frac{d^2x}{dt^2} + \frac{H^2e^2}{m} x = Xc$$

¹ *Phil Mag.*, September 1904.

² *Ibid.*, April 1911.

³ *Conduction of Electricity through Gases*, p. 220, 1906

Integrating from $x = 0$ to $x = d$, and putting $\frac{dx}{dt} = 0$ at $x = 0$ and at $x = d$, we get

$$\frac{1}{2} \frac{H^2 e^2 d^2}{m} = e \int_0^d X dx = V$$

where d is the distance from the strip to the electrode, and V the difference of potential between them. Hence—

$$\frac{e}{m} = \frac{2V}{H^2 d^2}$$

The assumption that $\frac{dx}{dt} = 0$ at $x = d$ means that the ion considered just reaches the electrode. Hence, if V is diminished, or H increased, then the ions do not get across to the electrode. Sir J. J. Thomson found 25 per cent got across with $V = 10$, $H = 19000$, $d = 0.3$ cm. Hence, for the 75 per cent stopped—

$$\frac{e}{m} \leq 60$$

The magnetic field had some effect with $V = 120$, so that some ions were present, for which

$$\frac{e}{m} = 720$$

For hydrogen ions in solutions $e/m = 9644$, so that if we assume the positive ions from the strip carry the same charge, we get for the atomic weights of these ions about 170 and 134. These results indicate that most of the ions consisted of atoms of platinum and some of oxygen, or nitrogen, atoms. Sometimes Sir J. J. Thomson found the current practically unaffected by the magnetic field, even when V was only one volt or less, which indicated that the ions were very heavy particles, probably platinum dust. It is clear, therefore, that at high temperatures some of the positive thermionic current may be carried by atoms of the hot metal, and some of it by the gas present. Rutherford (*vide supra*) also found heavy ions at high temperatures, besides others due to the air. At high pressures the current due to the gas is very large compared with that due to the metal.

Sir J. J. Thomson¹ also measured e/m for the positive ions

¹ *Conduction of Electricity through Gases*, p. 148, 1906.

from an iron wire at a very low pressure, and found it equal to 400, which makes the atomic weight 24 on the assumption that the charge is equal to that on an hydrogen atom in solutions.

O. W. Richardson¹ measured e/m for the positive ions emitted by platinum in a vacuum, and found $e/m = 384$. With carbon he got $e/m = 353$.

In Richardson's experiments the ions from a hot strip placed in a uniform electric field perpendicular to its surface were deflected by a magnetic field which was parallel to the length of the strip. The ions from the strip were received on a plane electrode perpendicular to the electric field. This electrode contained a slit parallel to the hot strip, and the number of ions which entered this slit was measured, as well as the total number. The electrode and slit could be moved in a direction perpendicular to the electric and magnetic fields. With no magnetic field the slit received a maximum fraction of the ions when it was opposite the strip, and with a magnetic field the position of this maximum was deflected through a distance which was determined

Let the distance from the strip to the electrode be d and the electric field Z . Then the time t taken by the ions to go a distance z in the direction of the electric field is $\sqrt{\frac{2mz}{Ze}}$. As they move across they are acted on by a sideways force Hev due to the magnetic field H . Here v denotes their velocity parallel to the electric field, so that $v = \frac{Zet}{m}$. If x denotes the deflection due to the magnetic field—

$$\frac{ZHe^2t}{m} = m \frac{d^2x}{dt^2}$$

which gives $\frac{HZe^2t^3}{6m^2} = x$ for $\frac{dx}{dt} = 0$ and $x = 0$ when $t = 0$. Putting

in $t = \sqrt{\frac{2md}{Ze}}$ and $Z = \frac{V}{d}$, this gives $x = \frac{Hd^2}{3} \sqrt{\frac{2e}{mV}}$, where V is the

P.D. between the strip and electrode.

In the above calculation we have neglected the force on the

¹ *Phil Mag.*, November 1908.

ion due to its motion in the magnetic field in the direction of x , but in Richardson's experiments the deflection x was small compared with d , so that this is allowable. In his experiments d was about 0.6 cm and x about 0.1 cm. V varied from 55 to 341 volts, and H from 1200 to 4670.

Richardson also measured e/m for the negative electrons from hot platinum in this way, and got it equal to 1.45×10^7 . Thus it appears that e/m for the positive ions emitted by iron, platinum and carbon in a vacuum was about 350 to 400 in these experiments. This gives about 26 for the atomic weight of these ions if we assume that they carry the same charge as a monovalent ion in solutions. It is evident, therefore, that they are not atoms of the hot substance. It seems likely that they may be sodium atoms, or molecules of carbon monoxide, which are nearly always present in vacuum tubes at low pressures, especially in the presence of large pieces of metal.

In a later paper Richardson and Hulbirt¹ give the results of measurements of e/m for positive ions from Pt, Au, Ag, Cu, Fe, Os, Ta, W, brass, nichrome and steel. For all these substances e/m came out nearly equal to 400.

Richardson and Brown² have made several sets of measurements on the kinetic energy and velocity distribution of the positive thermions similar to their measurements on the negative electrons, described in Chap. I. The results obtained in general agree with the kinetic theory, as in the case of the negative electrons.

The following table gives the values of the gas constant for one c.c. of any gas calculated from their observations on the variation of the positive thermionic current from a hot plate to a parallel electrode with the P.D., by means of the theoretical formula—

$$\log \frac{i'}{i} = \frac{Ne\varphi}{R\theta}$$

¹ *Phil. Mag.*, October 1910.

² *Ibid.*, December 1908, March 1909, October 1909.

DISCHARGE OF POSITIVE ELECTRICITY

Substance	Temperature.	Gas Constant/ 10^3
Platinum	1193	4.0
"	1067	3.5
"	1293	3.5
Gold (1)	(1030-973)	4.2
" (2)	(1190-1163)	3.9
Silver (1)	1020	3.0
" (2)	1150	2.9
Palladium	1170	3.4
Al Phosphate (1)	1230	3.9
" (2)	1170	3.4
Nickel	1120	3.6
Iron (1)	1100	4.6
" (2)	1100	5.2
" (3)	1240	4.4

The theoretical value of the gas constant for one c.c. under standard conditions is 3.7×10^3 . The values found in a few cases differ a good deal from the theoretical value, but, taken together, the results show that the average energy of the positive ions is nearly equal to that of a gas molecule at the temperature of the hot body, and also that the velocity distribution among the ions is that given by Maxwell's law.

When the initial current has disappeared there is little or no positive current in a good vacuum. In gases, however, a permanent positive thermionic current remains, which depends on pressure and nature of the gas.

The writer¹ found the following positive thermionic currents from a platinum wire at 1300° C in hydrogen —

Pressure	Current
766 mms.	40×10^{-9} amperes
156 "	24 " "
9 "	4 " "

These numbers indicate that at high pressures the current only increases slowly with the pressure.

In comparing the positive thermionic currents due to different gases, it is important to remember that the relative values change rapidly with the temperature. If Q in one gas is greater

¹ *Phil. Trans. A.* vol. 202, p. 243, 1903.

than in another, then the current due to the first gas may be negligible compared with that due to the second at low temperatures, but enormously greater at high temperatures. For example, Richardson found the current in hydrogen less than that in oxygen at 900° C, while the writer found the reverse to be the case at much higher temperatures. Also, Richardson found Q for nitrogen much greater than for oxygen, so that although in his experiments at about 800° C oxygen gave the greater current, it is clear that at higher temperatures the current in oxygen should be very small compared with that in nitrogen.

$$\text{The equation} \quad i = \frac{IF}{F + \frac{mV^2}{1.4\epsilon\lambda\sqrt{6\pi}}} \quad (\text{vide supra}),$$

since λ is inversely proportional to the gas pressure, shows that the electric force required to make i/I have a definite value is proportional to the pressure

Richardson¹ examined the positive thermionic current in hydrogen, and found that at 800° C it was 54×10^{-13} ampere on first letting in hydrogen to 27.5 mms pressure, but fell off after five hours' heating to only 21×10^{-13} ampere.

If we calculate Q from the current at 1300° C., and 9 mms. pressure, given above, and Richardson's final value at 800° C., we get $Q = 50,000$, which is of the right order of magnitude. At high temperatures the time required for the wire to get into a steady state is very much shorter than at low temperatures, so that in my experiments at 1300° C. the variation did not last more than a few minutes. Richardson found Q for the positive thermionic current in hydrogen at 1.9 mms. to be 35,800, and at 226 mms 57,000. These values are probably greater than those in oxygen, so that at high temperatures the positive thermionic current in hydrogen may be much greater than in oxygen, although at 800° C Richardson found it not more than one-twentieth as great.

O. W. Richardson (*loc. cit*) also examined the permanent positive thermionic current from platinum in several other gases.

¹ *Phil Trans A*, vol. 207, p. 1 1906

He found that the current (i) from platinum at 730° C. and 820° C. in oxygen could be represented by the equation—

$$i = \frac{\alpha p^{\frac{1}{2}}}{\beta + p^{\frac{1}{2}}}$$

where p denotes the pressure and α and β are constants. The following table is taken from his paper—

Pressure in mms. of Hg	i (calculated).	i (observed).
		$1 = 10^{-12}$ ampere
0.003	0.75	1.0
0.17	5.2	5.9
1.5	13.2	15
3.1	17.1	17
10.7	25	23.5
30	32.3	30
97	39.5	38
200	43.7	43
399	46.7	49.3
587	48.3	50.5
766	49	53.5

These numbers are for a wire at 820° C. The calculated values were got by taking $\alpha = 56$ and $\beta = 4$. When p is large, the current becomes nearly independent of p , and at 820° C. its maximum value is 2.5×10^{-10} amperes per sq. cm

At 1170° C. the currents agreed well with the equation—

$$i = \frac{\alpha p}{\beta + p}$$

where $\alpha = 38 \times 10^{-10}$ ampere, and $\beta = 4.8$ mms. of Hg. It appears, therefore, that when p is small i varies as p^n and that n increases considerably with the temperature.

Richardson explained the relation between i and p by the theory referred to on page 38.

The variation of the positive thermionic current with the temperature at constant pressure appears to agree in all cases with the formula $i = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, so that just as with the negative current in hydrogen, A and Q must be functions of the pressure, such as are consistent with

$$\frac{\alpha p^n}{\beta + p^n} = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$$

wh A 10 1 1 1

The data available, however, are not sufficient to test this conclusion. Since n increases with the temperature, we should expect Q to increase with the pressure. In oxygen at 2 mms. pressure Richardson found $Q = 3 \times 10^4$ and in air at 760 mms. $Q = 4.9 \times 10^4$. In hydrogen, also, as we have seen, Q for positive currents increases with the pressure.

Richardson also examined the positive thermionic current in nitrogen and helium. It increased with pressure in each case. At about 900°C the current in nitrogen was about one-tenth that in oxygen, while in helium it was about one-third that in oxygen.

Richardson gives the following table of values of Q —

Gas	Pressure, mms	Q for + ions	Q for - ions
O_2	2	3.04×10^4	13.55×10^4
Air	760	4.92 "	8.97 "
N_2	2.8	7.12 "	11.2 "
H_2	1.9	3.58 "	12.0 "
H_2	326	5.7 "	5.56 "

According to these numbers the ratio of the positive current in nitrogen to that in oxygen is proportional to $e^{-\frac{4.08}{29}} \times 10^4$, so that at high temperatures the current in oxygen should be negligible compared with the current in nitrogen. A series of determinations of the values of A and Q for platinum in oxygen and other gases at all pressures from 0 to 760 mms. would probably throw much light on the process of formation of the positive ions.

Richardson (*loc cit*) found that when the temperature or pressure is changed, the positive thermionic current in oxygen lags behind, showing that time is required for the platinum to get into equilibrium with the oxygen, just as with the negative current in hydrogen.

It will be observed that there is a close analogy between the negative thermionic current in hydrogen and the positive current in different gases. Both appear to be due to the presence of the gas in the surface layer of the hot solid, but the precise nature of the action is unknown. The fact that the current increases

regularly with the pressure at low pressures suggests that the gas dissolves in the platinum without forming a definite compound, for if a definite compound were formed, we should expect complete combination above its dissociation pressure, and complete decomposition below it. At higher pressures, since the leak becomes nearly independent of the pressure, chemical combination is suggested.

Sir J. J. Thomson¹ found that many salts when heated gave a large thermionic current. Phosphates of Al, Fe, Hg, Ca, Zn, Pb, Ag, Sn, all gave positive currents. With Al, Fe, and Hg phosphates the current was very large. Nitrates and chlorides also gave positive currents. Oxides gave an excess of negative ions, especially the alkaline earths.

Sir J. J. Thomson (*loc. cit.*) made the interesting discovery that when the same compounds were powdered in a mortar they acquired a charge of the opposite sign to that which they evolved on heating; the mortar and pestle, of course, got a charge of the opposite sign to the compound.

Sir J. J. Thomson suggested that the compounds are covered with an electrical double layer, and that those which, like aluminium phosphate, evolve positive ions when heated and become negative when rubbed, have the positive charge in the layer on the outside. The oxides, he suggested, have the negative charge on the outside, and rubbing or heating removes some of the outside layer. The layers, of course, may contain molecules of the surrounding gas. On this view, the escape of the ions at high temperatures is a kind of evaporation.

Garrett² determined e/m for the ions emitted by aluminium phosphate. He found 10 per cent. of the ions had $e/m=9700$, which shows that they were probably hydrogen atoms. He found that when the phosphate is moistened with water the production of ions is greatly increased until the water is all driven off by heating.

F. Horton³ examined the spectrum of the gas evolved by a platinum strip coated with aluminium phosphate, when it was

¹ *Proc. Camb. Phil. Soc.* vol. xiv. p. 105, 1907.

² *Phil. Mag.*, October 1910.

³ *Proc. Roy. Soc. A.* vol. 84, p. 433, 1910.

heated strongly in a vacuum This substance was found by Sir J. J. Thomson to give a large positive thermionic current

Horton found that the spectra of oxygen and carbon were always present, and concluded that the carriers of the thermionic current were carbon monoxide molecules It is well known that carbon monoxide is very often present in vacuum tubes, especially in the presence of considerable masses of metal, which always evolve CO when put in a vacuum. In Richardson's experiments on e/m for the positive ions emitted by various metals, CO was, no doubt, present, so that it seems possible that some of the carriers may have been CO.

In Sir J. J. Thomson's experiments the aluminium phosphate emitted a copious supply of positive ions when heated in air at atmospheric pressure. In this case there could not have been any CO present, so that it is clear that the positive ions are not always CO They are probably formed from any substance present, and a constituent of the salt seems much the most probable

Horton¹ examined the thermionic current from hot platinum coated with sodium phosphate. At 800° C. in oxygen and CO he found it increased with the pressure up to about 3 mms of mercury and then diminished about 25 per cent. from 3 mms to 8 mms. The positive thermionic current in oxygen at 800° C was about ten times smaller than in carbon monoxide. In hydrogen at 800° C the positive thermionic current did not diminish with the pressure above 3 mm, but remained nearly constant. It was about ten times larger in hydrogen than in carbon monoxide. As already mentioned, the relative values of the currents in different gases depend very greatly on the temperature, since Q depends on the nature of the gas and on its pressure

Horton found that the current in oxygen diminished with long-continued heating, whereas in CO it increased rapidly on first admitting the gas These results, on the whole, support the view that the carriers are CO molecules in some cases.² With clean platinum in pure hydrogen they are no doubt hydrogen atoms, or

¹ *Proc. Cam. Phil. Soc* vol xvi p 89, 1910.

² Davison finds that the positive ions from salts are not molecules of the gases present — *Phil. Mag.*, January 1912.

molecules, and in pure oxygen, oxygen atoms, or molecules. If any sodium is present it no doubt helps to supply the carriers.

Platinum and most other substances disintegrate or splutter to a greater or less extent when heated to a high temperature in gas at low pressure. This effect depends greatly on the nature of the gas. It is greater with platinum in oxygen than in nitrogen or hydrogen.

When the hot body is spluttering, some of the thermions get attached to the minute particles coming off, and so become very large ions, which have a very small velocity due to an electric field.

The fact that the spluttering depends on the gas suggests that it may be connected with the formation and decomposition of unstable compounds at the surface of the hot body.

The spluttering of the cathodes in vacuum tubes is very analogous to the spluttering of hot bodies. It also depends on the gas, for example, aluminium does not splutter in ordinary gases, but does in helium, argon, and other monatomic gases. Since helium and argon do not combine chemically with other elements, this seems to show that the spluttering of cathodes is not connected with ordinary chemical action.

The positive thermionic current from platinum in hydrogen or nitrogen at high temperatures is greater than in oxygen, but the spluttering is greater in oxygen than in hydrogen.

G. Owen¹ made a series of experiments on the nuclei for cloudy condensation emitted by a hot platinum wire in air, and in hydrogen. He found these nuclei were unaffected by an electric field. They are probably molecules of platinum, and are bigger, he found, the higher the temperature.

If the dust given off by hot platinum in air is allowed to accumulate in the air near the platinum, many of the ions emitted get attached to dust particles, which may make it impossible to saturate the current, even when the electrodes are near together. This can be prevented by passing a rapid current of air between the electrodes, so as to blow out the dust particles, as was done in my experiments described at the beginning of this chapter.

¹ *Phil. Mag.*, September 1903.

So far as can be judged at present, there does not seem to be any very intimate connection between the disintegration of platinum and the thermionic current from it

Beattie found that various mixtures of substances when heated to between 300°C and 400°C . emit ions which are usually mostly positive. For example, a mixture of sodium chloride and iodine on a zinc plate gives a copious supply of positive ions at 350°C

Garrett and Willows found that zinc chloride, bromide and iodide give off positive ions when heated to a few hundred degrees. They found the velocity of the ions emitted to be about 0.060 cms per sec for one volt per cm in air at atmospheric pressure. These ions produce a cloud when passed over water. Garrett in a further investigation concluded that the production of these positive ions is due to chemical action and is similar to the production of the ions found in newly prepared gases and in the fumes from phosphorus. It therefore falls outside the province of this book.

CHAPTER VI

THE CONDUCTIVITY OF THE BUNSEN FLAME

A BUNSEN coal-gas flame is a good conductor of electricity. If two platinum electrodes are placed in such a flame, so that they get red hot, and are connected to a battery, the current between them can be easily measured with a galvanometer. Fig 7 shows a convenient apparatus for experiments of this kind.

A brass tube AB, about 5 cms. in diameter and 70 cms long, is mounted horizontally on a wooden stand, as shown. The end B is closed with a cork, while at A a gas jet is fixed so as to send

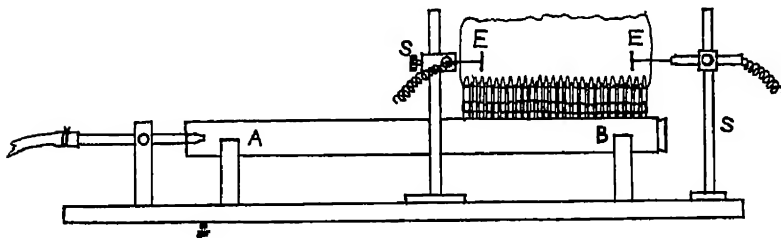


FIG. 7

a stream of coal gas down the tube. Twenty-five small brass tubes, each about 6 mms. in diameter and 15 mms long, are soldered into a row of holes 1 cm apart along the upper surface of the large tube, near the end B. To each of these a fused quartz tube about 3 cms. long is attached with a short piece of indiarubber tubing. The quartz tubes should all be as nearly as possible equal and of the same internal diameter as the small brass tubes. This arrangement will act like a Bunsen burner, and gives a flame about 26 cms. long and 7 cms. high. The jet at A should be supported so that its distance down the tube can be adjusted and the diameter of the jet be so chosen as to give a non-luminous

flame with a well-defined inner cone on each quartz tube. A jet about 2 mms. in diameter will probably be nearly right.

Two vertical platinum discs E, E, about 1.5 cms in diameter, made of thick foil, welded to platinum wires about 1 mm thick, form convenient electrodes. The wires can be fused into glass tubes and supported on small adjustable stands SS, as shown. One of the electrodes may be supported near one end of the flame, and the stand for the other made to slide in a groove parallel to the flame, so that the electrodes can be easily placed at any distance apart. The platinum wires should be long enough to prevent the ends of the glass tubes getting too hot.

The following table gives the currents observed¹ with such an apparatus ($I = 8.8 \times 10^{-9}$ ampere).—

Potential Difference	Distance between Electrodes				
	1 cm	4.5 cm	9 cm	13.5 cm	18 cm
600 volts	310	304	295	280	270
400 "	255	247	240	230	215
200 "	175	170	165	155	143
120 "	130	125	115	104	90
40 "	67	64	57	53	48
20 "	42	39	35	32	29
10 "	22	20	16	14	13
4 "	9	8	7	6	5.3
2 "	5	4.7	4	3.5	3

It will be seen that in every case the current falls off slowly with increasing distance between the electrodes. When the distance between the electrodes is small the current (C) is nearly proportional to the square root of the potential difference (V), provided this is greater than three or four volts. Fig. 8 shows the relation between the current and potential for two electrodes 1 cm. apart in an ordinary Bunsen flame. One of the electrodes was a platinum disc 3 cms in diameter, and the other a disc 1 cm in diameter, surrounded by a guard ring 3 cms in diameter. The curve drawn is the parabola $C = 19.25\sqrt{V}$.

If one of the electrodes is moved so near the edge of the flame

¹ H. A. Wilson, *Phil. Mag.*, October 1905

that it becomes less hot, the current is greatly diminished, especially if the cooler electrode is negative

The conductivity of an ordinary Bunsen flame can be measured

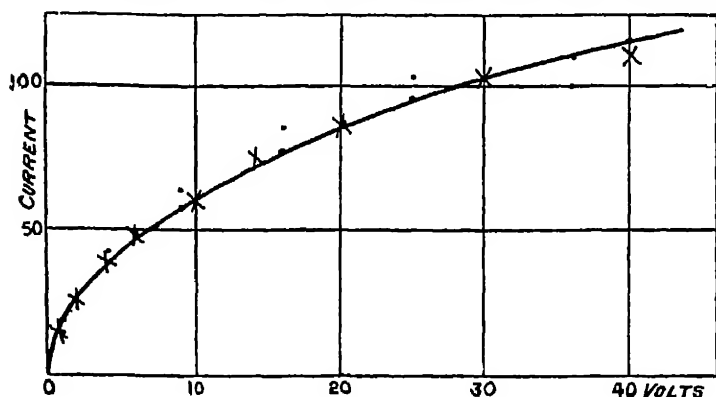


FIG. 8

between horizontal electrodes one above the other, consisting of platinum wire gauze. The gauze should not have more than three or four wires per centimetre, so that the flame can pass freely through it

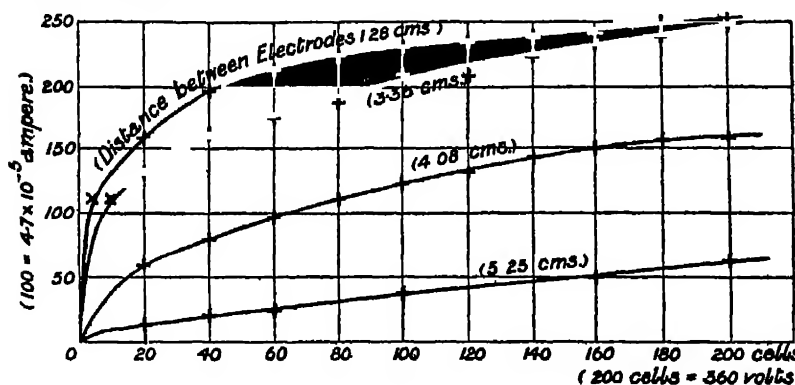


FIG. 9.

Fig. 9 shows the relation between the current and P.D. obtained in this way,¹ the lower electrode being negatively charged and about 2 cms. above the burner.

¹ H. A. Wilson, *Phil. Trans A* vol 192, p 499, 1899

Fig 10 shows the relation between the current and distance between the gauze electrodes

The current was almost independent of distance up to 3 cms. but then fell off rapidly. This was mainly due to the upper electrode getting cooler when near the top of the flame. If the upper electrode was kept at a nearly constant temperature, by passing a current through it, the current was nearly independent of the distance, right up to the top of the flame. With horizontal gauze electrodes the current of gas carries up a continuous large supply of ions between the electrodes from below them, so that we should expect a large current to be obtained, even with the electrodes very close together

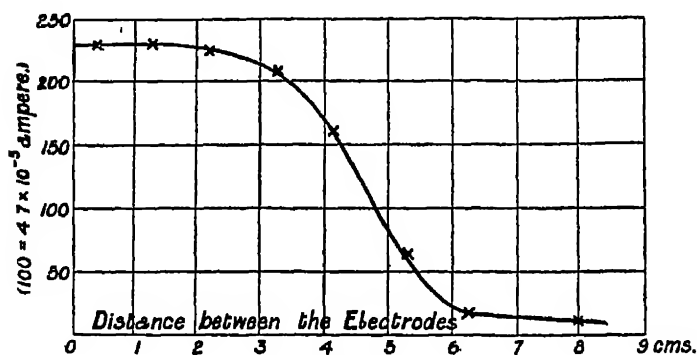


FIG. 10

The variation of the potential along the flame from one electrode to the other was examined¹ by means of a fine platinum exploring wire, connected to an electrostatic voltmeter or quadrant electrometer. The voltmeter was connected to one of the electrodes and to the wire. The wire was perpendicular to the line joining the electrodes, and could be moved along the flame from one electrode to the other. Since the flame is a conductor and the wire insulated, it takes up the potential of the flame at the place where it is put in.

Fig. 11 shows the variation of the potential obtained in this

¹ H. A. Wilson, *Phil. Trans. A.* vol. 192, p. 499, 1899; *Phil. Mag.*, October 1905. Marx, *Ann. der Phys.* vol. 14, p. 2, 1900

way with the electrodes 17.7 cms. apart, and a P.D of 550 volts between them

It will be seen that there is a uniform potential gradient except near to the electrodes. Near the negative electrode there is a large fall of potential, and a small one close to the positive electrode. Such a variation of the potential is characteristic of conduction through flames, and always occurs when both the electrodes are hot. If one of the electrodes is moved near to the edge of the flame, so that it becomes cooler, the fall of potential near it increases. In this way nearly all the drop of potential can be concentrated at either the positive or negative electrode.

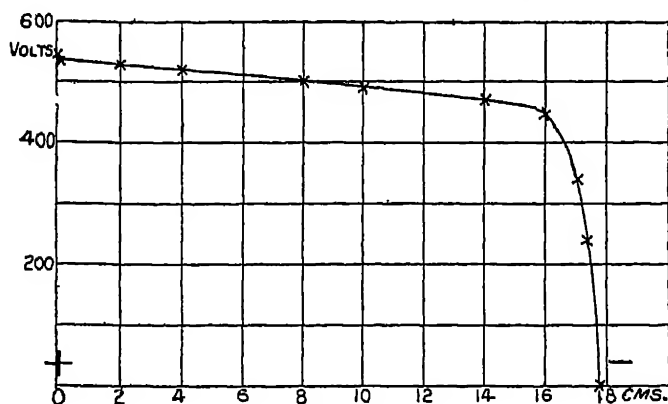


FIG 11

The uniform gradient between the electrodes is proportional to the current. This was shown by using two exploring wires, kept at a constant distance apart and connected to an insulated quadrant electrometer. The following numbers were obtained in this way¹

Current (C) $1 = 8.8 \times 10^{-9}$ amperes	P D between exploring wires.	P D - c
270	4.0 volts	0.015
54	0.8 "	0.015
18	0.25 "	0.014

The exploring wires were 0.5 cm. apart.

H. A. Wilson, *Phil. Mag.*, October 1905.

Mr E. Gold¹ found the uniform gradient proportional to the current between the limits 5×10^{-6} ampere and 260×10^{-6} ampere. In his experiments the current was increased by putting alkali salts, such as potassium carbonate, on the negative electrode, but the salt vapour did not extend into the part of the flame where the exploring wires were put in. It appears, therefore, that at a distance from the electrodes the flame obeys Ohm's law. In Mr. E. Gold's experiments, the ratio of the potential gradient in volts per centimetre to the current in amperes was 0.70×10^6 . The cross-section of the flame was about 2 sq. cms., so that the specific resistance of the flame was 1.4×10^5 ohms per c.c. In my experiments just mentioned the specific resistance was about 2×10^5 ohms per c.c. The specific resistance of a Bunsen flame varies greatly with the composition of the mixture of coal gas and air.

The fall of potential in the uniform gradient between the electrodes is equal to Acd , where c is the current, d the distance between the electrodes, and A a constant. When d is small, Acd can be neglected compared with the total fall of potential (V), and then $V = Bc^2$ approximately, as we have seen. In any case, therefore, the equation—

$$V = Acd + Bc^2$$

represents the relation between the current, potential difference, and distance between the electrodes. The numbers given in the table *supra* are represented approximately by this equation with $A = 0.03$ and $B = 0.0061$. The term Bc^2 is equal to the fall of potential near the electrodes.

If n_1 denotes the number of positive ions per c.c. in the flame, e_1 the charge on each ion, v_1 the velocity with which they are moving in the direction from one electrode to the other, and n_2 , e_2 and v_2 denote the corresponding quantities for the negative ions, then the current per sq. cm. (i) is given by the equation—

$$i = n_1 e_1 v_1 + n_2 e_2 v_2.$$

The velocity of an ion through a gas is proportional to the strength of the electrical field (X), so that if the gas is flowing

¹ *Proc Roy Soc. A* vol 79, 1907.

towards the negative electrode with velocity u , we have

$$\begin{aligned}v_1 &= k_1 X + u \\v_2 &= k_2 X - u\end{aligned}$$

where k_1 and k_2 denote the velocities of the ions relative to the gas in unit field.

Hence— $i = n_1 e_1 (k_1 X + u) + n_2 e_2 (k_2 X - u)$.

Take the axis of x perpendicular to the surfaces of the electrodes, and suppose that everything is constant over planes parallel to the electrodes, then

$$\frac{dX}{dx} = 4\pi (n_1 e_1 - n_2 e_2).$$

In the uniform gradient between the electrodes $\frac{dX}{dx} = 0$, so that $n_1 e_1 = n_2 e_2$, and therefore

$$i = n_1 e_1 X (k_1 + k_2)$$

and is therefore independent of the velocity of the flame gases

Comparing this with the equation $V = A dx + B e^2$, we see that

$$i / X = 1 / A a = n_1 e_1 (k_1 + k_2)$$

where a is the cross-section of the flame

Thus, the fact that the flame at a distance from the electrodes obeys Ohm's law, shows that the velocities of the ions in it are proportional to the strength of the electric field.

The theory of the relation between the current and the potential difference in an ionized gas is given by Sir J. J. Thomson in his book on *The Conduction of Electricity through Gases*, chap. iii, and I shall only give here a short discussion of some points which apply particularly to conduction through flames

In nearly all cases of the conduction of electricity through gases the charge on a positive ion is equal to the charge on a negative ion. If we assume that this is the case in flames, we obtain

$$\frac{dX}{dx} = 4\pi (n_1 - n_2) e \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{and} \quad e n_1 (k_1 X + u) + e n_2 (k_2 X - u) = i \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where u is the velocity of the gas in the direction of x

These equations give

$$n_1 e = \frac{1}{k_1 + k_2} \left\{ \frac{v}{X} + \frac{(k_2 X - u)}{4\pi X} \frac{dX}{dx} \right\} \quad (3)$$

$$n_2 e = \frac{1}{k_1 + k_2} \left\{ \frac{v}{X} - \frac{(k_1 X + u)}{4\pi X} \frac{dX}{dx} \right\} \quad (4)$$

Let the positive electrode be at $x = 0$ and the negative at $x = l$. In the case where $u = 0$ close to the positive electrode we have $n_1 = 0$, because the positive ions all move towards the negative electrode, while at the negative electrode $n_2 = 0$. Hence, from (3) and (4), in this case—

$$\left. \begin{aligned} k_2 &= -8\pi v \left/ \left(\frac{dX^2}{dx} \right) \right|_{x=0} \\ k_1 &= 8\pi v \left/ \left(\frac{dX^2}{dx} \right) \right|_{x=l} \end{aligned} \right\} \quad (5)$$

These equations enable k_1 and k_2 to be easily calculated from the variation of X near the electrodes, but only rough estimates can be got in this way, because it is impossible to measure X very exactly close to the electrodes

The corresponding equations when u is not zero can, of course, be easily obtained, but are of no value.

If the electrodes are made of horizontal wire gratings to allow the flame to flow through them, it is evident that u is not zero, and also that n_1 and n_2 cannot be put equal to zero at the positive and negative electrodes, respectively, because the flame gases contain ions which are carried through such electrodes. The distribution of electric force near such electrodes will not be the same as near plane electrodes, except at distances from them greater than the distance between the wires forming the grating. Thus, the equations (5) ought not to be applied to results obtained with grating electrodes.

In flames when both electrodes are hot the variation of the electric force is much larger near the negative than near the positive electrode. This is shown clearly in Fig 11. The equations (5) show that this means that the velocity of the negative ions is much larger than the velocity of the positive ions¹

Close to the negative electrode the current must be carried by

¹ H. A. Wilson, *Phil Trans A* vol. 192, p 499, 1899.

the positive ions, so that the electric force is large there, owing to the small velocity of these ions. At the positive electrode the current is carried by negative ions having a high velocity, so that the force there is only slightly greater than in the uniform gradient

The variation of the potential shown in Fig 11 is represented fairly well, except close to the positive electrode, by the equation—

$$V = 540 - 4.44x - 462e^{-81.7(l-x)}$$

Using this equation to calculate $\left(\frac{dV}{dx}\right)_{x=l}$ we get by (5)

$k_1 = 14$ cms per sec for one volt per cm., which, of course, is subject to a large possible error. This appears to be the only estimate yet made of the velocity of the positive ions in a Bunsen flame free from salt vapours. The gases present in such a flame are N_2 , H_2O , CO , CO_2 , etc. An ion consisting of CO_2 would probably have a velocity of about 40 cms. per sec.,¹ which is of the same order as that just found. There seems, therefore, no reason to doubt that the positive ions in a Bunsen flame free from salt consist simply of charged molecules of the gases present.

The variation of the potential gradient near the positive electrode is too slight to enable k_2 to be estimated in this way, but it is clear that it must be of a much higher order of magnitude.

Let q denote the number of fresh ions of either sign produced per c.c. per sec., and consider a layer of thickness dx perpendicular to the x axis. Inside one sq. cm. of this layer qdx fresh positive ions are produced per sec., and $\alpha n_1 n_2 dx$ positive ions disappear by recombination, α being the coefficient of recombination. The number of positive ions entering the layer due to the electric field

is $k_1 X n_1$, so that in a steady state, when $\frac{dn_1}{dt} = 0$, we have

$$\frac{d}{dx}(k_1 X n_1) = q - \alpha n_1 n_2 \quad . \quad . \quad . \quad (6)$$

In the same way for the negative ions—

$$-\frac{d}{dx}(k_2 X n_2) = q - \alpha n_1 n_2 \quad . \quad . \quad . \quad (7)$$

¹ See p. 86.

(1), (6), and (7) give

$$\frac{d^2X^2}{dx^2} = 8\pi e (q - \alpha n_1 n_2) \left(\frac{1}{k_1} + \frac{1}{k_2} \right) \quad (8)$$

It follows from (1) and (8) that in the uniform potential gradient between the electrodes, $n_1 = n_2 = n$ and $q = \alpha n^2$. Hence—

$$i = Xen (k_1 + k_2) = Xc (k_1 + k_2) \sqrt{\frac{q}{\alpha}}$$

Equation (8) shows that $\frac{d^2X^2}{dx^2}$ is positive when the ionization q is greater than the recombination $\alpha n_1 n_2$. In the layers near the electrodes there must be an excess of ionization over recombination, because in the uniform gradient X_0/k_1 positive ions per sq. cm. flow past per sec, away from the positive electrode, and X_0/k_2 negative ions away from the negative electrode. Thus d^2X^2/dx^2 must be positive near each electrode, so that the curve giving the relation between X^2 and x must be convex to the x axis near the electrodes. Consequently, the electric force rises as either electrode is approached. Since k_2 is much greater than k_1 the excess of ionization over recombination is much greater near the negative electrode than near the positive, so the variation in X near the negative electrode is much greater than near the positive electrode.

If k_2 is very large compared with k_1 then the current will be nearly equal to Xen_2/k_2 except close to the negative electrode, where $n_2 = 0$ and the current is equal to Xen_1/k_1 in any case. The theory of the distribution of the electric force between the electrodes can be greatly simplified¹ when k_2 is large compared with k_1 by assuming that the current is equal to Xen_2/k_2 , but this assumption obviously fails close to the negative electrode.

Equations (3), (4), and (5), when $u = 0$, give

$$\frac{k_2 n_2}{k_1 n_1} = \frac{\left(\frac{dX^2}{dx} \right) x = l - \frac{dX^2}{dx}}{\left(\frac{dX^2}{dx} \right) x = 0 - \frac{dX^2}{dx}}$$

Since $\left(\frac{dX^2}{dx} \right)_{x=0}$ is nearly zero, we have, approximately,

¹ J. J. Thomson, *Conduction of Electricity through Gases*, chap. 111.

$$\frac{k_2 n_2}{k_1 n_1} = \frac{\left(\frac{dX^2}{dx}\right)_x = l}{\frac{dX^2}{dx}} - 1$$

With $V = 540 - 4.44x - 462e^{-1.87(l-x)}$ this gives the following numbers—

$l - x$	$k_2 n_2 / k_1 n_1$
0 cms.	0
0.1 „	0.45
0.5 „	5.3
1.0 „	39

It appears, therefore, that in the case shown in Fig 11 the current carried by the positive ions is half the total current one millimetre from the negative electrode, and one-fifth five millimetres from it, but at one cm away it is only 3 per cent. Most of the fall of potential occurs within one cm. of the negative electrode, so that it is clear that the variation of the potential near the negative electrode cannot be accurately calculated by assuming that $i = Xen_2k_2$. J J Thomson¹ found that the variation of the potential near the negative electrode, calculated on the assumption that $i = Xen_2k_2$, does not agree with that observed.

We have seen that near the negative electrode the excess of ionization over recombination is equal to $k_2 n X_0$, where n is the number of negative or positive ions per c.c. in the uniform gradient, and X_0 the electric force there. This number of negative ions is produced per sec. in a layer next to the negative electrode of thickness λ_2 , where $q\lambda_2 = k_2 n X_0$.

If, following J J Thomson, we assume that in this layer no recombination takes place, and that outside it the electric force is uniform and equal to X_0 , then the fall of potential in the layer can be calculated. It comes out proportional to i^2 . Near the positive electrode we may imagine a similar layer of thickness $\lambda_1 = \frac{k_1 n X_0}{q}$ in which also the drop of potential is proportional to i^2 . In the uniform gradient the fall of potential is proportional to the current and to the distance between the electrodes, so that $V = Alc + Bc^2$,

¹ *Conduction of Electricity through Gases*, p. 235, 1906

which is the equation which we have seen represents the experimental results satisfactorily

The ratio of λ_1 to λ_2 is equal to k_1/k_2

In the curve shown in Fig 11 the potential gradient is uniform up to about 2 cms. from the cathode, and less than 1 mm. from the anode. If we suppose these distances to represent λ_2 and λ_1 we see that k_2 must be at least twenty times k_1 . This method of estimating k_2/k_1 was used by Marx¹. It is clearly too inaccurate to have any value for the assumption that recombination does not take place inside the layers cannot be true in flames, and the width of the layers cannot be estimated at all accurately.

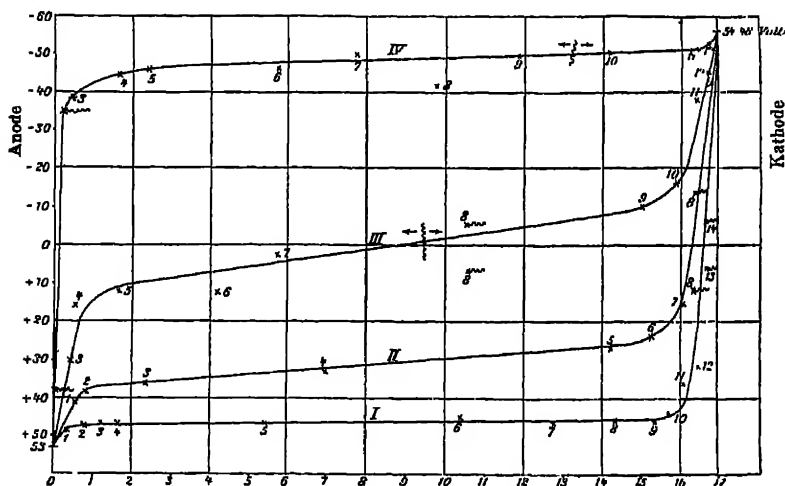


FIG 12

Inside the Bunsen flame the fall of potential between the electrodes always consists of large drops near the electrodes, with a small gradient between. If one of the electrodes is much colder than the other, the greater drop takes place at the colder electrode, whether it is positive or negative. Fig 12, given by Marx,² shows how the shape of the potential curves for two horizontal electrodes depends on the temperature of the positive electrode. Its temperature was altered by raising the electrodes in the flame, keeping the distance between them constant

¹ Loc. cit.

² Loc. cit

In the uniform gradient $q = an^2$, so that none of the ionization there contributes to the current. It is clear, therefore, that the current is always far from saturation when there is a uniform gradient in the middle and sudden drops of potential near the electrodes. On the layer theory $(\lambda_1 + \lambda_2)/l$ is the ratio of the actual current to saturation current.

The current between the two hot parallel plates in the flame does not diminish appreciably, even when the distance between them is altered from, say 2 cms to 1 mm, which shows clearly that the current is very far from its saturation value at the larger distance. It would be interesting to make experiments on the variation of the current with the distance between the electrodes at very small distances.

Hot electrodes in a Bunsen flame must emit ions which will help to carry the current at the surface of the electrodes. The fraction of the current carried by these ions is usually small. It is easy to see that if the negative electrode emitted $k_2 n X_0$ negative ions per sec., the drop of potential near that electrode would disappear, and the uniform gradient would extend right up to it. Since this does not happen, even when very small currents are passed through the flame,¹ it is clear that the thermionic current is relatively very small.

F. L. Tufts² found that coating the negative electrode with lime caused the potential drop there to nearly disappear. This is evidently due to the large emission of negative electrons by hot lime.

¹ E. Gold, *Proc. Roy. Soc. A* vol. 79, 1907.

² *Phys. Zeitsch.* vol. v. p. 76, 1904.

CHAPTER VII

THE ELECTRICAL CONDUCTIVITY OF SALT VAPOURS

THE presence of the vapour of a metallic salt in a Bunsen flame increases its conductivity. Salts of the alkali metals of large atomic weight give a specially big effect. This effect can be conveniently studied qualitatively with the apparatus described at the beginning of the last chapter. If the two electrodes are placed about 1 cm apart, and a bead of potassium carbonate on a platinum wire held below them so that the vapour from it fills up the flame between the electrodes, the current due to any P D is increased probably several thousand times.

If the electrodes are placed further apart the effect of the salt vapour in different parts of the space between the electrodes can be easily tried. It is found that the current is not appreciably changed unless the salt vapour is put in close to the negative electrode.

At the positive electrode, and anywhere between the electrodes, there is no effect, but if the salt vapour comes in contact with the negative electrode, a very large increase in the current is produced.

If the electrodes are connected to an alternating P D. and some potassium carbonate placed on one of them, a galvanometer in the circuit will indicate a current in the direction from the electrode without salt to the other, for the flame will practically allow no current to flow in the opposite direction.¹

If salt is put on the negative electrode, so that a large current is obtained, then on putting in a bead of potassium carbonate in some other part of the flame between the electrodes, it is found that the current is increased, and that the current is nearly inversely proportional to the length of the flame left free from salt. Thus, if two-thirds of the distance between the electrodes is filled with salt vapour, the current is about trebled.

¹ H. A. Wilson, *RI Lecture*, February 1909.

With K_2CO_3 on the negative electrode, the current diminishes as the distance between the electrodes is increased. This is shown in Fig 13. Roughly speaking, the current is inversely proportional to the distance between the electrodes so long as the positive electrode does not come into contact with the salt vapour from the negative electrode.

Coating the negative electrode with lime acts in the same way as putting salt on it, which was discovered by Tufts¹ before the similar effect due to salt was observed.²

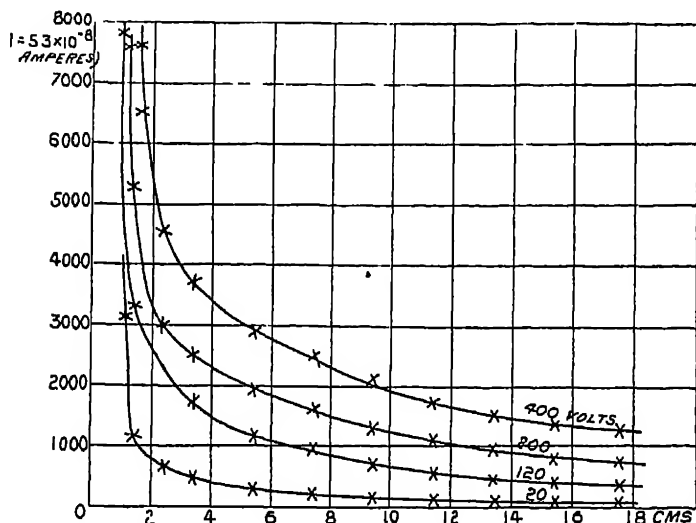


FIG 13.

Fig 14 shows the distribution of potential between the electrodes with potassium carbonate on the negative electrode.

Comparing this with Fig 11, it will be seen that the drop of potential at the negative electrode is much diminished, and the uniform gradient correspondingly increased.

If the two exploring wires are placed in the uniform potential gradient in the flame, and connected to an insulated quadrant electrometer, the gradient, as we have seen in the previous chapter, is proportional to the current, showing that the flame

¹ F. L. Tufts, *Phys. Zeitschr.* vol. v. p. 76, 1904.

² H. A. Wilson, *Phil. Mag.*, October 1905.

away from the electrodes, when free from salt, obeys Ohm's law. If a bead of salt is put just below the two wires, so that they are both in the salt vapour, the P.D. between them becomes practically zero, although without salt on the negative electrode the current is not appreciably affected. This shows clearly that the salt vapour is a much better conductor than the flame by itself.

In one experiment of this kind the principal electrodes were 18 cms. apart, and the uniform gradient, as indicated by the exploring wires and electrometer, was 1.6 volts per cm. with a P.D. of 700 volts between the main electrodes. The current gave a galvanometer deflection of 200 mms. with no salt on the negative

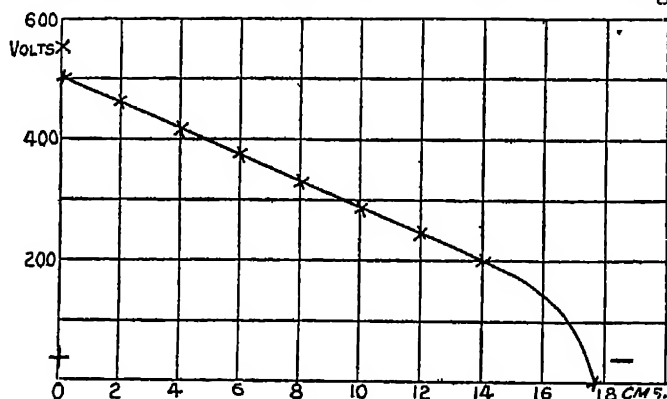


FIG. 14.

electrode. On putting a bead of potassium carbonate below the exploring wires the electrometer deflection became zero, while the current was unchanged. In the equation

$$V = A\delta c + Bc^2$$

the term Bc^2 represents the fall of potential at the electrodes, and $A\delta c$ the fall in uniform gradient. In this experiment $A\delta c = 18 \times 1.6$ volts, so that $Bc^2 = 700 - 29 = 671$ volts. Now, the salt vapour occupied about 2 cms. of the flame, so that when it was put in the fall in the uniform gradient was diminished by $2 \times 1.6 = 3.2$ volts. Bc^2 must, therefore, have been increased by 3.2 volts; that is, by one in two hundred. The current c , therefore, ought to have been increased by one in four hundred, or from 200 to 200.5. But in these experiments the flame is never

perfectly steady, so that the galvanometer deflection always oscillates slightly, so that so small an increase could not have been detected. In this way it is easy to explain the fact that although the salt vapour is a much better conductor than the flame, yet it has no effect on the current, except at the negative electrode. The reason is that since nearly all the fall of potential takes place close to the negative electrode, that is, that practically all the resistance to the passage of the current is close to this electrode, increasing the conductivity of the rest of the flame is practically without effect.

When salt is put on the negative electrode the drop of potential there is greatly diminished, so that the distribution of

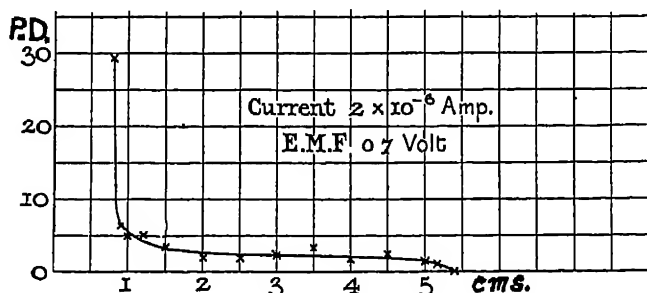


FIG 15

potential is changed to a nearly uniform potential gradient from one electrode to the other, that is, the resistance is nearly uniformly distributed. In this case, if a part of the flame is filled with salt vapour, the total resistance is nearly proportional to the length left free from salt, so that the current is nearly inversely proportional to this length.

If the positive electrode is moved to the end of the flame, so that it becomes much cooler than the negative electrode, the fall of potential takes place mainly at the positive electrode, and then, as we should expect, the current is increased when salt is put on the positive electrode, but not when it is put on the negative electrode.

Fig. 15 shows the distribution of potential with potassium carbonate on the negative electrode for a total P.D. of 0.7 volt

and Fig 16 that with potassium carbonate on both electrodes, but not in the space between the electrodes. These two figures are taken from a paper by E Gold¹

When the flame is completely filled with salt vapour the distribution of potential between the electrodes becomes again similar to that in a flame free from salt, the current being, however, much greater for a given potential difference.

For experiments on flames filled with salt vapour, it is best to use a method devised by Gouy². A salt solution is sprayed by means of compressed air, and the air and spray are mixed with coal gas, so that the mixture gives a Bunsen flame uniformly

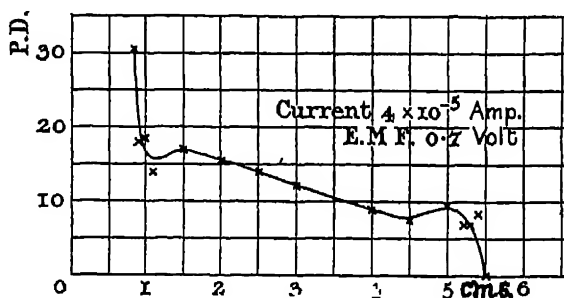


FIG 16.

filled with salt vapour. Fig. 17 shows the apparatus used by the writer³ in one series of experiments

Carefully regulated supplies of coal gas and air were mixed together, along with spray of salt solution, and the mixture burnt from a brass tube 0.7 cm. in diameter. The air supplied by the water pump P partly escapes by bubbling through mercury in B, and then passes into a carboy A. From A the air passes through a flask W containing water, to the sprayer S, and its pressure is measured by the water manometer M. The air supply is regulated by means of a pinch-cock K, and by altering the water supply to the pump

The coal gas was passed through a regulator R into a gasometer H, from which it passed through a constriction L into the globe

¹ *Proc Roy Soc A.* vol 79, 1907

² *Ann de Chimie et de Phys.* [5], t. xviii, p. 25

³ *Phil Trans Roy Soc A.* vol 192, pp. 499-528, 1899

G, where it mixed with the air and spray. The gas pressure was indicated by a manometer M'. The mixture passed into a globe G', where the coarser spray settled, and then to the flame F.

With an apparatus of this kind a very steady flame containing definite amount of salt vapour can be obtained. The amount of salt in the flame is proportional to the strength of the solution used.

The relation between the current and potential difference has been examined in flames filled with alkali salt vapours by Arrhenius,¹ Smithells,² Dawson and the writer, and by the writer.⁴

Arrhenius measured the current between two vertical parallel

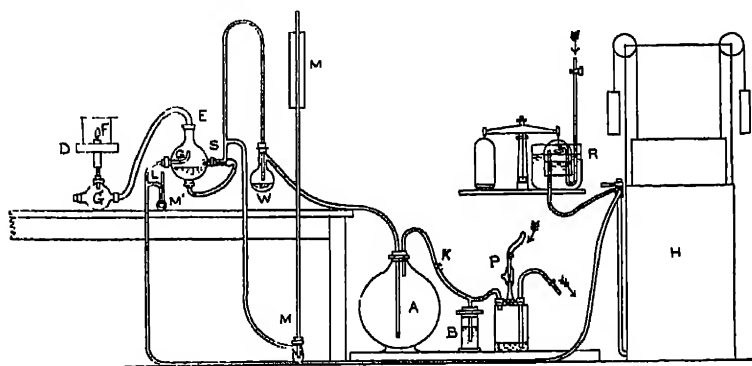


FIG 17

platinum electrodes. He found that the relation between the current and P.D. could be expressed approximately in all cases by the equation $C = A\sqrt{K}f(V)$, where A is constant, depending on the metal, but the same for all salts of any one metal, the concentration in gram molecules per litre of the solution sprayed, and $f(V)$ denotes a function of the P.D. between the electrodes, which has the same values for all salts. Thus, with constant P.D., the current was proportional to the square root of the amount of salt in the flame.

Arrhenius' electrodes were 0.56 c.m. apart, so that we should

¹ *Wied. Ann.* vol. xlii, 1891. ² *Phil. Trans. A* vol. 193, p. 89, 1899.

³ *Phil. Trans. A* vol. 192, p. 499, 1899.

expect the term Ac^2 in the equation $V = Ac^2 + Bc^2$ to be small compared with Bc^2 when c is not too small.

Consequently for large values of V we should expect $f(V)$ to be proportional to \sqrt{V} , so that $c = A\sqrt{KV}$.

The following table contains Arrhenius' results for potassium iodide, the unit of current being 10^{-8} ampere. The currents are the difference between the current with salt and that without any

E M F in Clark's Cell	Concentration of Solution						
	Normal = 1	$\frac{1}{2}$	$\frac{1}{10}$	$\frac{1}{100}$	$\frac{1}{250}$	$\frac{1}{500}$	$\frac{1}{1000}$
1	540	248	120	52.2	20	6.0	2.7
2	616	284	139	59.9	23	7.9	2.9
5	734	360	174	75.8	29.1	10.1	3.7
10	1009	464	225	99.7	37.4	13.0	4.7
20	1340	616	298	130	49.6	17.2	6.3
40	1920	811	427	186	71.2	24.8	9.0

An examination of these numbers shows that the current varies rather more rapidly than \sqrt{K} , and that it is nearly proportional to \sqrt{V} when V is greater than that due to two cells. Arrhenius found that the conductivity of the alkali salt vapours in the flame increased rapidly with the atomic weight of the metal.

The fact that all salts of any one metal gave equal currents was explained by Arrhenius by supposing that they were all converted into hydroxides by the water vapour present in the flame.

Arrhenius' results were confirmed and extended by Smithells, Dawson, and the writer (*loc. cit.*). The current was measured between two concentric cylinders with their axis vertical in a Bunsen flame containing salt vapour.

The inside cylinder was hotter than the outside one, and a current was always obtained when the electrodes were connected to the galvanometer without any battery in the circuit.

Fig. 18 shows the relation between the current, from the inside to the outside cylinder, and P.D. when a $\frac{1}{10}$ normal solution of potassium nitrate was sprayed.

It will be seen that the current is much greater when the

outside cylinder is negative than when it is positive. Since $V = Bl^2$ approximately, where i is the current density at the negative electrode, we get $V = Bc_1^2/(2\pi r_1 l)^2$ and $V = Bc_2^2/(2\pi r_2 l)^2$, where l is the length of the cylinders, r_1 the radius of the outside one, r_2 that of the inside one, and c_1 the current with the outside cylinder negative, and c_2 that with the inside cylinder negative. Hence $c_1/c_2 = r_1/r_2$. For the cylinders used, r_1/r_2 was about 2, whereas in the above diagram c_1/c_2 for 5 volts is about 3, but the calculation assumes the two cylinders to be at the same temperature.

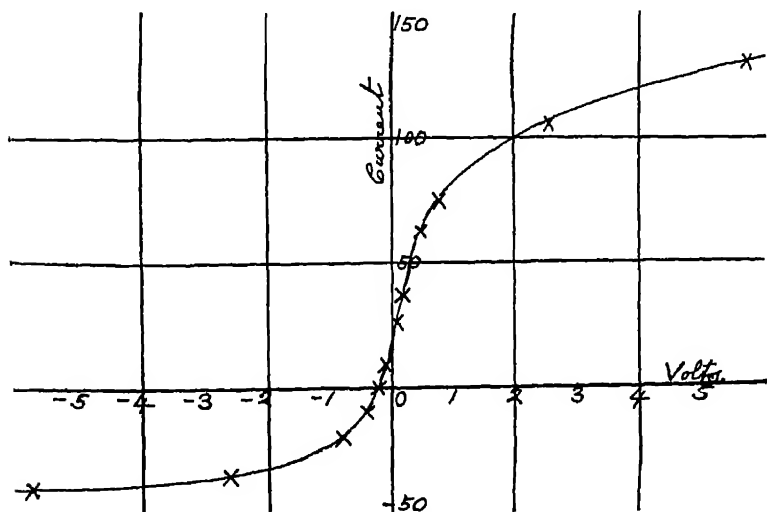


FIG. 18

When the P.D. was zero, there was a current from the inside cylinder to the outside one. This shows, of course, that the equation $V = Aic + Bc^2$ cannot be true in this case, when V is very small. The explanation of this current is probably as follows. The negative ions in the flame have a much higher velocity than the positive ions, so that they diffuse more quickly. Consequently an insulated electrode immersed in the flame acquires a small negative potential sufficient to make the rate at which negative ions fall on it equal to the rate at which positive ions fall on it. This potential is greater the higher the temperature. Consequently the outside cylinder tends to take up a higher potential

than the inside one. The hot electrodes in the flame emit ions, and this emission is probably increased by the salt vapour. If an electrode is emitting negative ions it will tend to acquire a positive charge, so that there may be an effect due to this cause in the opposite direction to that due to diffusion. These effects, however, are small, and can usually be neglected when the potential difference between the electrodes is above two or three volts.

The relation between the current and P.D. for small P.D.'s is

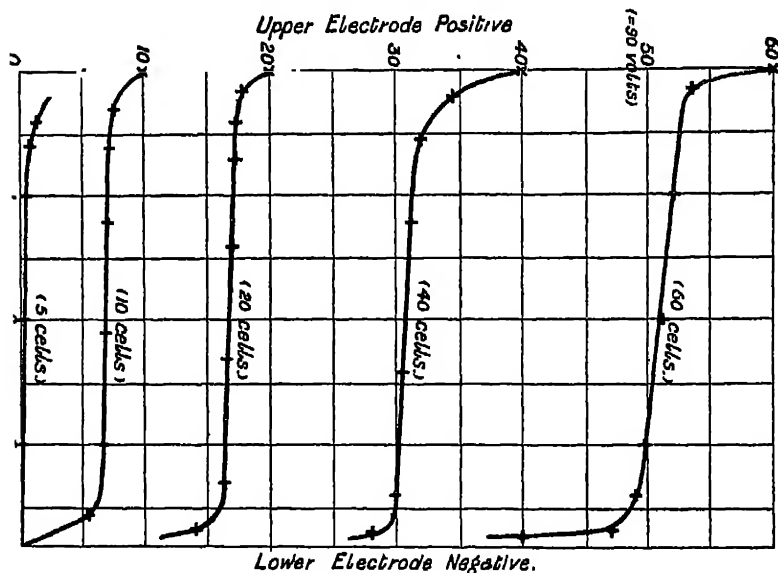


FIG. 19

complicated by such effects as those just mentioned, which are difficult to allow for accurately.

The distribution of potential between the electrodes¹ in a flame containing rubidium chloride is shown in Fig 19. The electrodes were horizontal wire gratings.

It will be seen that the uniform gradient is very small, although the current with 120 volts was about 2×10^{-4} ampere. The lower electrode consisted of a gauze with wires 3 mms. apart, while the upper one had wires about 1 mm. apart. The upper electrode was cooler than the lower one

¹ H. A. Wilson, *Phil Trans A* vol 192, p 507, 1899

Fig 20 shows the change in the distribution of potential when the upper electrode is changed from positive to negative. With the lower one positive, there is no drop near to it. The lower electrode, which was very hot in these experiments, therefore must have emitted a thermionic positive current, for otherwise there ought to have been a small drop at it.

In these experiments the upward current of the flame gases carries a continuous supply of ions up through the lower electrode. Consequently, if the lower electrode is positively charged it will attract the negative ions from the gas as they pass through it, so that the gas will acquire a positive charge. The theory of the variation of the potential near the electrodes is complicated by this supply of ions from below.

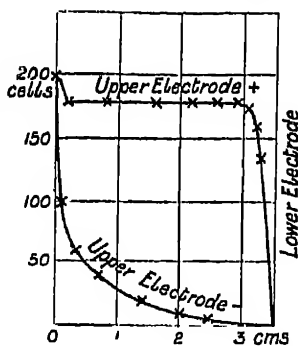


FIG 20.

Marx¹ made estimates of the order of magnitude of the ionic velocities in flames containing salt vapours, by applying the theory of the variation of the potential near plane electrodes in a gas at rest to his observations with horizontal coarse grating electrodes in the flame. He made use of J. J. Thomson's layer theory, described in a previous chapter. The results are of little value, owing to the theory used not applying when the ionized gas is streaming through grating electrodes. Moreover, the method is of little use, even in cases to which the theory does apply. Marx's lower grating had wires 3 mm apart, and he used measurements of the potential taken up by a wire parallel to the grating, made at distances from the grating as small as 0.35 mm. At such distances from the grating the lines of flow of the current must have been nearly normal to the surface of the grating wires, and so not perpendicular to the exploring wire. Also the effective area of the electrodes must have been more nearly equal to the area of the surface of the wires than to the area of the grating. In view of these considerations, I do not think Marx's experiments

¹ *Ann. d. Phys.* vol. iv. p. 2, 1900.

can be regarded as giving even the order of magnitude of the ionic velocities.

All that can be deduced from the distribution of potential between the horizontal grating electrodes is that when both are equally hot the velocity of the negative ions is probably considerably larger than that of the positive ions, for the variation of the potential near the negative electrode is more rapid than near the positive electrode.

THE VELOCITY OF THE IONS OF SALT VAPOURS IN FLAMES

The velocity of the positive ions of alkali salt vapours in flames was estimated by the writer¹ by finding the potential gradient required to make them move down the flame against the upward stream of gases. The apparatus used is shown in Fig. 21

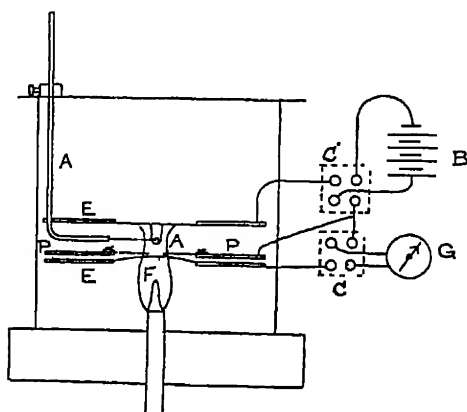


FIG. 21

- F Flame inside glass cylinder, resting on wooden block W. and covered with metal plate T
- EE Grating electrodes.
- PP Screen above lower electrode
- AA Bead of salt and support
- CC' Commutators
- B Battery.
- G Galvanometer.

¹ *Phil Trans. A* vol 192, p. 499, 1899.

A bead of salt was put in the flame just below the upper electrode, and the current from the lower electrode measured. It was found that when the upper electrode was positive, introducing the bead caused no increase in the current unless the potential difference between the electrode was greater than 100 volts, when the electrodes were 5 cms. apart. When the upper electrode was negative, other conditions being the same, the current was increased on introducing the bead, even with one or two volts.

To prevent any ions reaching the lower electrode by passing down the sides of the flame, where the velocity of the gases is

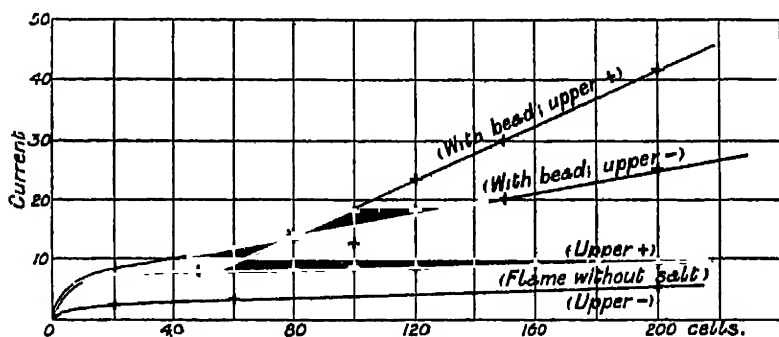


FIG. 22.

small, a screen was placed above the lower electrode. This was of platinum gauze, with a hole in the middle 2 cms. in diameter. This hole was filled up by the flame, which also passed through the gauze around the hole. The lower electrode was bent up so that it was only 2 or 3 mms. below the screen. The screen was connected to the battery, so that the galvanometer only received the current going through the hole in it to the lower electrode.

Fig. 22 shows the results obtained with a bead of potassium carbonate. It will be seen that the bead did not appreciably increase the current when the upper electrode was positive, unless the P.D. was above about 100 volts. The P.D. required to increase the current with the upper electrode positive was found to be about 100 volts for all salts of caesium, rubidium, potassium, sodium, and lithium. The possible error in the necessary P.D. was rather large, especially in the case of sodium and lithium,

which only gave a small increase, even with large potentials. The value 100 volts was probably correct within 20 per cent. The potential gradient in the upper part of the space between the electrodes was found to be 3.3 volts per cm. without any salt, when the P.D. was 100 volts. The introduction of the salt lowers the potential gradient in the part of the flame filled with salt vapour to practically zero, so that it increases the fall of potential in the rest of the flame.

In the present case, if the salt vapour occupied 2 cms. of the flame it would increase the fall of potential at the negative electrode by 6.6 volts. The drop at the negative electrode was 84 volts, so that since the current is proportional to the square root of the drop, the current ought to have been increased by 3.3 in 84, or 4 per cent. The current was eight scale divisions, so that this increase could not be detected. Since the uniform gradient in the absence of salt is proportional to the current, it must have been increased by 4 per cent to 3.31 volts per cm. Obviously, the gradient which is required is that just below the salt vapour, and not that in it, which is very small.

The average velocity of the gases in the burner tube was found to be 206 cms. per second from the volume passing through. The diameter of the flame was about 2.5 cms, which indicates a cross-section about thirteen times that of the tube. Owing to the rise of temperature, an expansion of about eight times might be expected, but gas enters the flame along its sides. Since the pressure of the gas in the tube is very nearly equal to atmospheric pressure, it seems clear that the velocity in the flame must be practically the same as that in the tube, in spite of the change of volume, because there is no pressure difference available to change the velocity. Hence we get for the apparent velocity of the positive ions of any alkali salt due to one volt per cm.

$$\frac{206}{3.3} = 62 \frac{\text{cms}}{\text{sec.}}$$

It has been assumed so far that if the positive ions move down the flame they will increase the current, and the fact that an increase is observed above a definite P.D. was supposed to justify this assumption. The precise way in which the current is increased remains to be considered.

In the uniform gradient the current, as we have seen,¹ is independent of the velocity of the gases, and given by

$$i = Xen(k_1 + k_2).$$

When the salt is put in the uniform gradient in the salt vapour is given by

$$i' = X'en'(k_1' + k_2')$$

where X' is very small compared with X and n' large compared with n ; k_1' and k_2' are probably of the same order as k_1 and k_2 . Hence, at the critical P.D.—

$$Xn(k_1 + k_2) = X'n'(k_1' + k_2').$$

At the edge of the salt vapour X changes to X' , so that there will be a layer of charge in the gas there. The positive ions of the salt do not move down at the critical P.D., so that below the salt X must be practically unaltered, as we have seen

If now the P.D. is slightly increased, the positive salt ions move down slowly. As they go down they will continually recombine with the negative flame ions present, and continually be reionized. Thus the conductivity of the flame below the salt will now be increased, and when the salt ions get to the negative electrode they will accumulate there and diminish the fall of potential. The increase of the current, it will be observed, is almost entirely due to the effect of the positive ions on the drop of potential at the negative electrode, and not to the increase in the conductivity in the uniform gradient

The maximum possible increase of the conductivity in the uniform gradient below the salt vapour can be easily calculated. Suppose the current without salt is i_0 , and with salt i , and let X_0 be the minimum gradient required to make the positive ions move down. Then, below the salt the gradient cannot be less than X_0 , so that the conductivity below the salt cannot be increased more than in the ratio i/i_0 , for X_0 is the gradient when the ions just do not move down, and therefore is equal to the gradient in the free flame corresponding to i_0 . Consequently, just above the critical P.D., the concentration of the salt ions moving down must be extremely small, but they accumulate at the negative electrode, and so produce an appreciable effect there.

¹ See p. 63.

It appears, therefore, that the salt ions which move down are not charged ions all the time, but must be continually recombining and reionizing. Since they produce an effect when they get to the lower electrode, it is clear that they must differ from the flame ions, so they cannot be hydrogen ions. It is natural to suppose that they are atoms of the alkali metal as in salt solutions. Suppose that a particular metal atom is ionized for a fraction f of the time, then if it just moves down the flame this means that $f(k_1 X - u) = (1 - f)u$ or $f k_1 X = u$, where u is the velocity of the flame gases, for while the atom is not charged it will be carried upwards with velocity u . It appears, therefore, that the quantity determined in the experiment described is $f k_1$ and not k_1 . It is convenient to call $f k_1$ the apparent velocity of the positive salt ions.

This experiment has been repeated by Mr. Lusby.¹ He found that the critical P.D. was 62 volts for all salts of alkali and alkaline earth metals. The distance between his electrodes was only 3 cms, which, unfortunately, was not enough to allow the uniform gradient to be well developed in the absence of salt, for the space occupied by the negative drop was over 2 cms. With the salt in, he observed a very small gradient for nearly 2 cms below the upper electrode, which was evidently due to this part of the flame containing salt vapour. He found the uniform gradient without salt to be 6.5 volts per cm., and the velocity of the flame to be 206 cms. per sec. This gives

$$k_1 f = \frac{206}{6.5} = 32 \frac{\text{cms.}}{\text{sec.}}$$

which agrees as well as could be expected with the value of $62 \frac{\text{cms.}}{\text{sec.}}$ I found, for his uniform gradient was too short (0.2 cm.) to be measured at all exactly. He used the value of the gradient found with salt vapour² to calculate $k_1 f$, but this is obviously incorrect. What is required is the gradient just below the salt vapour, which, since the current is the same, should be the same as without salt.

Moreau³ estimated the apparent velocity of the positive ions

¹ *Proc Camb. Phil Soc* vol. xvi. part 1. 1910

² Lusby got $k_1 f = 300 \frac{\text{cms.}}{\text{sec.}}$ by using the gradient found with salt in. A very minute trace of salt vapour is enough to greatly diminish the gradient

of sodium and potassium salts by finding the potential gradient required to make them move across the flame from the bottom of one vertical electrode to the top of another. In this way he found $k_1 f = 80$ cms per sec, which agrees well with 62 cms. per sec.

Marx's estimate of the order of magnitude of $k_1 f$ has already been discussed. He found $k_1 f$ to be about 250 cms. per sec, which is of the same order as 60.

The mean of 32, 62, and 80 is $58 \frac{\text{cms.}}{\text{sec.}}$, which may be taken to be the most probable value of $k_1 f$ and is probably correct within 50 per cent., $k_1 f$, of course, must vary in different flames, and in different parts of the same flame.

If the positive ions consist of atoms of the metal, we should expect k_1 to be nearly inversely proportional to the square root of the atomic weight of the metal.

Now, the conductivity due to a definite amount of salt increases rapidly with the atomic weight, so that f must be much smaller for lithium than for caesium. If we suppose that when the concentration of the salt vapour is very small f is proportional to the square root of the atomic weight of the metal, and k_1 inversely proportional, then the product $k_1 f$ would be constant, as is found to be the case.

It is probable¹ that for caesium f is nearly unity,² so that, assuming this, we get the following values of k_1 —

	Atomic Weight	k_1
Caesium	133	58
Rubidium	85.4	72
Potassium	39.2	107
Sodium	23.1	139
Lithium	7.0	253

I think it is more probable that these numbers are too large than too small. The value of k_1 to be expected on the kinetic theory can only be estimated very roughly, because the necessary data as to the free path of the ion, etc, have to be guessed at, in the flame.

¹ H. A. Wilson, *Phil. Mag.*, June 1911.

² If f for caesium is less than unity then the values of k_1 will be corre-

The temperature of a Bunsen flame is above the melting-point of platinum, because very thin wires will melt in it, so that it cannot be much below 2000°C . Estimates made by putting in thermocouples are, of course, too low, because the couple radiates, and so does not take up the true temperature. According to the kinetic theory, we have $k_1 = 2\sqrt{\frac{3}{2\pi}} \frac{e\lambda}{mV}$, where e is the charge on the ion, λ its mean free path, m its mass, and V the square root of the mean square of its velocity of agitation.

The flame contains N_2 , H_2O , CO , H_2 , etc. Of these N_2 is present in the largest quantity. The free path of a nitrogen molecule in nitrogen at 0° and 760 mms. is $9.5 \times 10^{-6}\text{ cm.}^1$ At 2000°C this gives $7.9 \times 10^{-5}\text{ cm}$. The free path of an atom of caesium is probably smaller than that of a molecule of nitrogen, so that I shall take the free path of a caesium atom in the flame to be $4 \times 10^{-5}\text{ cm}$. The velocity of agitation of a hydrogen molecule at 0°C . is $1.84 \times 10^5\text{ cms. per sec.}$, so that for a caesium atom at 2000°C . we get

$$V = 1.84 \times 10^5 \times \sqrt{\frac{2273 \times 2}{273 \times 133}} = 6.5 \times 10^4.$$

Also e/m for a caesium atom carrying the same charge as a hydrogen atom in solutions is equal to 72.5 in electromagnetic units.

Hence, we get $k_1 = 1.4 \frac{e\lambda}{mV} = \frac{1.4 \times 72.5 \times 4 \times 10^{-5} \times 10^8}{6.5 \times 10^4}$

$= 6.3 \frac{\text{cms.}}{\text{sec.}}$ for one volt per cm. This is nearly ten times smaller than the value 58 found for caesium on the assumption that f' is unity for this metal, but the data used in the calculation of k_1 , and also the formula employed are so doubtful that no weight can be attached to the discrepancy. The experimental result and the theoretical value are of the same order of magnitude, which is all that could be expected.

I think, therefore, that there is no reason to doubt that the positive ions of alkali salt vapours in flames are atoms of the metal, as in solutions. This view is powerfully supported by the fact discovered by Lenard that the yellow coloration of the

¹ Meyer's *Kinetic Theory of Gases*, p. 192.

flame by sodium salts is attracted by a negatively charged electrode in the flame.

If two platinum wires are put in a Bunsen flame, one above the other, and some sodium carbonate is put on the upper one, then if the wires are connected to a battery giving a few hundred volts, or to an induction coil, sodium light appears at the lower wire when it is the negative pole, but not when it is positive.¹ This clearly shows that the positive ions contain the metal, and effectually disposes of the suggestion that the positive ions of salt vapours in flames consist of hydrogen atoms. If they were hydrogen atoms it would be difficult to explain the increase in the current above the critical P.D., for hydrogen atoms going down would not increase the conductivity at the negative electrode. Moreover, salt vapours enormously increase the conductivity of the cyanogen flame, which contains no hydrogen.²

The velocities of the ions of salt vapours in air at about 1000° C. was estimated by the writer,³ using a method similar to that used in the flame. A mixture of air and spray of salt solution was passed through a platinum tube heated to a bright red heat in a gas furnace. The P.D. required to make the ions of the salt vapour move against the stream of hot air on emerging from the tube was found in the same way as in the flame.

In this case there was practically no current until the critical P.D. was reached, so that the potential gradient could be taken to be uniform without serious error. The critical P.D. was found to be 25 volts for the positive ions of all the alkali salts, and 48 volts for salts of Ca, Sr, and Ba. For the negative ions of all salts of alkali metals and alkaline earth metals the critical P.D. was 7 volts.

The velocity of the air current was 160 cms per sec., so that the apparent ionic velocities were—

(1) Negative ions	20	$\frac{\text{cms.}}{\text{sec.}}$
(2) Positive ions of alkali metals	7.2	$\frac{\text{cms.}}{\text{sec.}}$
(3) Positive ions of alkaline earth metals	3.8	$\frac{\text{cms.}}{\text{sec.}}$

¹ H. A. Wilson, *R.I. Lecture*, February 12, 1909.

² Smithells, Dawson and Wilson (*loc. cit.*).

³ *Loc. cit.*

The possible error in these experiments was large, and the values obtained can only be regarded as giving the order of magnitude of the velocities.

The free path of an air molecule in air at 0° C. and 760 mms is 9.6×10^{-6} cms. At 1000° C this becomes 4.5×10^{-5} cms. For a caesium atom carrying the same charge as a monovalent ion in solutions $e/m = 72.5$, and

$$V = 1.84 \times 10^5 \times \sqrt{\frac{1273 \times 2}{273 \times 133}} = 4.9 \times 10^4.$$

If we assume that the free path of the caesium atom is one-half that of an air molecule, we get

$$k_1 = \frac{1.4 \times 72.5 \times 2.3 \times 10^{-5} \times 10^8}{4.9 \times 10^4} = 4.8 \text{ cms. per sec}$$

for one volt per cm. This agrees as well as could be expected with the value 7.2 found if we assume that for caesium f is about unity. For the lighter metals we may suppose that f is smaller than unity, as in flames.

The distribution of the electric force in flames shows that the velocity of the negative ions must be much larger than that of the positive ions. The writer and others¹ attempted to find the velocity of the negative ions by the same method as was used for the positive ions, and results varying from 1000 to more than 10,000 were obtained. When the upper electrode is negatively charged, putting in the salt increases the current, even with small potential differences. Fig. 23 shows the results obtained by the writer.²

It will be observed that the current with salt increases rapidly at about one volt, and it was supposed, therefore, that this was the critical P.D. The current, however, is very considerably increased by the salt, even with zero P.D.

When the upper electrode is negatively charged there is a large potential drop at it, and a uniform gradient between the electrodes, which is proportional to the current and independent of the velocity of the gas. When salt is put in near the upper electrode the large drop there is diminished, and so the uniform gradient and the current must be increased, whether the

¹ Moreau and E. Gold.

² *Phil. Trans. A.* vol. 192, 1899.

CONDUCTIVITY OF SALT VAPOURS

negative ions move down the flame or not. Thus the method used for the positive ions is not applicable to the negative ions and the supposed determinations of the velocity of the negative ions made by it are of no value. Indirect determinations, which will be discussed in later chapters, show that the velocity of the negative ions is about 10,000 cms. per sec. for 1 volt per cm. This is about what we should expect if the negative ions were free electrons.

The free path of an electron in nitrogen at 2000° C. may

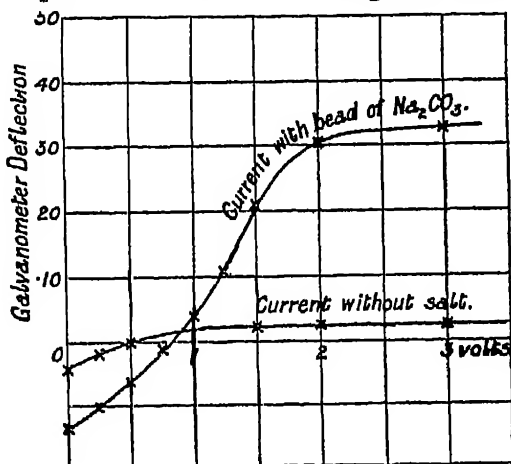


FIG. 23.

taken to be about 31.6×10^{-5} cm., that is, four times the free path of a nitrogen molecule. The velocity of agitation is

$$V = 1.84 \times 10^6 \times \sqrt{\frac{2273 \times 2 \times 1.8 \times 10^3}{273}} = 3.2 \times 10^7.$$

Taking $e/m = 1.75 \times 10^7$, we get

$$k_2 = \frac{1.4 \times 1.75 \times 10^7 \times 31.6 \times 10^{-5} \times 10^8}{3.2 \times 10^7} \\ = 24,400 \text{ cms. per sec. for 1 volt per cm.}$$

Probably the actual free path is shorter than 31.6×10^{-5} cm., account of the attraction between the electron and the molecule.

If we take $k_2 = \frac{1}{2} \frac{e\lambda}{mV}$ instead of $1.4 \frac{e\lambda}{mV}$ we get $k_2 = 8700$.

If the positive ions of alkali salts in flames consist of me

atoms, and the negative ions of free electrons, as seems probable, then the ionization most likely consists in the expulsion of an electron from an uncharged atom of the metal. Or a molecule of the hydrate, like KOH, may combine with an atom of hydrogen, forming water and K, which at the moment of its liberation emits an electron. The precise way in which the ions are formed can only be guessed at.

Note—The theoretical formula $k = \frac{1}{m} \frac{e\lambda}{V}$ was first obtained by Sir J. J. Thomson. Langevin, by allowing for the variation of λ , got $k = e\lambda/mV$. The writer,¹ allowing also for the variation of V , got $1.4e\lambda/mV$. The value of λ is probably diminished by the action of the charge on the surrounding molecules.² In the case of heavy ions the velocity is probably really greater than $e\lambda/mV$ on account of the persistence of the velocities after collisions.³ Sir J. J. Thomson⁴ has given a theory according to which the velocity of a heavy ion is nearly independent of its mass and charge, and depends practically only on the surrounding gas. Calculations of k by means of the formula $k = e\lambda/mV$ are therefore of little value, and cannot be relied on to give more than the order of magnitude to be expected.

RELATIVE CONDUCTIVITIES OF DIFFERENT ALKALI SALTS IN FLAMES

The conductivities imparted to a Bunsen flame by salts of the alkali and other metals were examined by Arrhenius (*loc. cit.*). He found that the conductivity was the same for all salts of any one metal, and was nearly proportional to the square root of the concentration of the salt solution sprayed. The conductivity increased rapidly with the atomic weight of the metal.

Smithells, Dawson and the writer (*loc. cit.*) confirmed Arrhenius' results, but found that when the concentration of the salt vapours was greater than the concentrations used by Arrhenius, that then all salts of the same metal did not give equal conductivities, and

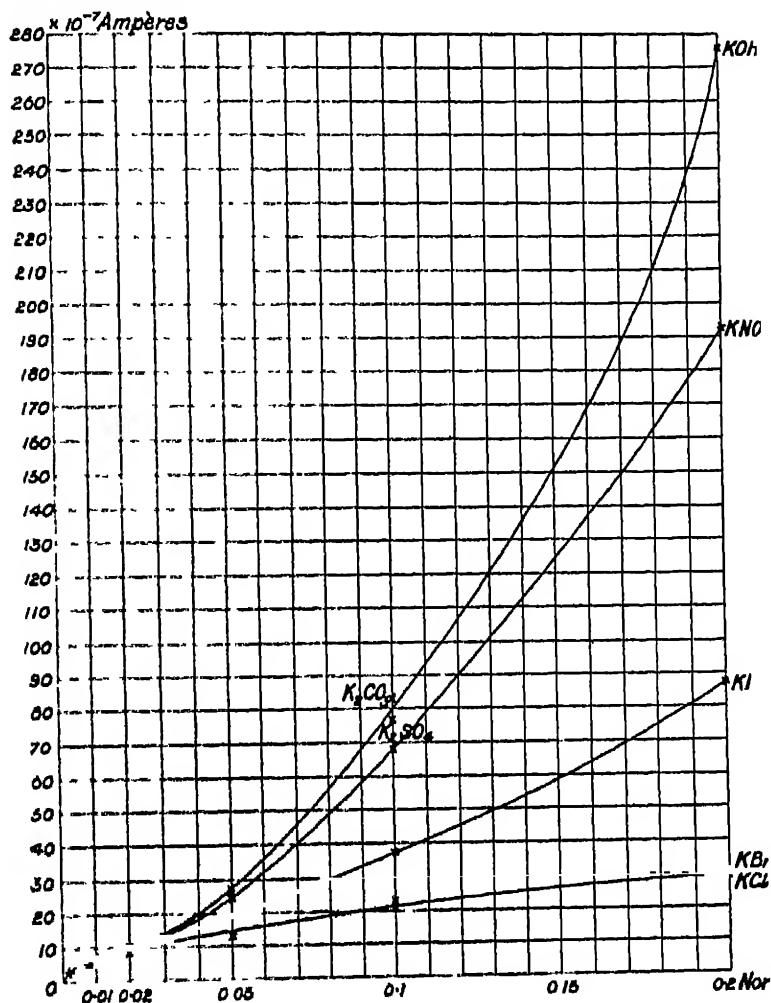
¹ *Phil. Mag.*, November 1910.

² Langevin, *Thèses*, Paris, 1902. Wellisch, *Phil. Trans. A.* vol. 109, 1909.

³ Jeans, *Kinetic Theory of Gases*.

⁴ *Proc. Camb. Phil. Soc.* vol. xv. part iv. 1909.

that then the conductivity was not always nearly proportional to the square root of the concentration.



Variation of current with concentration of solution. E.M.F., 5.60 volt

FIG. 24.

Fig. 24 shows the variation of the current due to 5.60 volt between concentric cylindrical electrodes, with the concentration (%) of the solution employed.

It will be seen that for concentrations up to about $\frac{1}{50}$ normal (a normal solution contains one gram molecule per litre) all the salts of potassium gave equal currents. Above this concentration the current due to oxysalts increased more rapidly than that due to halogen salts. For small concentrations the current is nearly proportional to the \sqrt{C} in all cases. In the case of potassium chloride and potassium bromide the current is proportional to \sqrt{C} up to the largest concentrations tried, but for the oxysalts this does not hold.

The following tables contain the currents observed with three potential differences for a large number of solutions. These currents are the means of the currents in opposite directions. The current through the flame without salt was subtracted in each case from the current observed when the solution was sprayed. The unit of current is 10^{-7} amperes

Concentration of solution	EMF	KCl	KBr	KClO ₃	KI	KNO ₃	$\frac{N}{2}$ -K ₂ SO ₄	$\frac{N}{2}$ -K ₂ CO ₃	KOH
2 normal	5.60	31.9	31.4	30.5	86.5	193	..	.	276
	.795	18.9	20.1	16.8	43.2	70.8	82.6
	.227	7.34	7.32	6.62	12.8	21.6		.	26.6
1	5.60	21.0	21.4	...	37.8	68.3	83.3	76.4	
	.795	12.4	12.4	...	21.3	29.3	33.4	35.4	
	.227	5.75	5.74	..	6.2	9.35	11.0	11.2	
0.5	5.60	14.1	14.7	12.9	22.8	24.5	27.5	27.6	24.1
	.795	9.23	10.3	8.35	12.8	13.2	13.8	14.2	12.8
	.227	4.0	4.13	3.81	4.6	5.1	5.71	5.43	5.1
0.2	5.60	8.93		10.2			
	.795	6.09			.	6.63			
	.227	2.97			.	3.15			
.01	5.60	6.02	6.97	6.77	6.99	7.06	6.33	6.00	6.1
	.795	4.27	4.90	4.69	4.78	4.84	4.56	4.30	4.05
	.227	2.17	2.23	2.32	1.97	2.47	2.30	2.20	1.86
.005	5.60	5.47	5.27			
0.02	5.60	...	4.03	...	3.89	3.73	
	.795		2.80	..	2.73	2.59	
	.227		1.50	.	1.24	1.45	

Concentration of solution	E M F	NaF	NaCl	NaBr	NaI	NaNO ₃	$\frac{N}{2}$ Na ₂ SO ₄	$\frac{N}{2}$ Na ₂ CO ₃	NaOH
.5 normal	5.60	8.98	7.66	9.24	12.5	.	12.6	11.4	12.0
	.795	1.78	5.37	5.38	5.83	.	6.64	6.60	6.20
	.227	2.00	2.07	2.11	2.21	.	2.49	2.45	2.61
.2	5.60	1.03	1.54	5.56	6.72	5.73	5.99	5.67	
	.795	2.65	3.14	3.32	3.36	3.77	3.75	3.64	
	.227	1.39	1.42	1.41	1.39	1.85	1.61	1.71	
.1	5.60	.	3.49		.	3.88	.	3.78	
	.795	..	2.45		.	2.67	.	2.65	
	.227	.	1.15		.	1.30	..	1.30	
.05	5.60	2.91	2.95	3.76	..	.	3.09	3.02	3.00
	.795	2.08	2.21	2.50	.	.	2.16	2.12	2.07
	.227	.98	1.05	.9796	.97	.98

Concentration of solution.	E M F	LiCl	LiNO ₃	RbCl	RbNO ₃	CsCl	CsNO ₃	HCl
.5 normal	5.60	1.88	2.28		.			1.08
	.795	1.09	1.59					
	.227	.56	.8935
.1	5.60	1.29	1.47	41.4	213.0	123	303	
	.795	.87	.99	26.4	82.4	60.5	115	
	.227	.41	.53	11.3	25.9	22.2	36.6	
0.2	5.60		.	14.8	19.4	17.6	20.1	
	.795	.	.	9.65	11.6	11.7	13.1	
	.227	...		4.71	5.14	5.9	6.2	
0.01	5.60	..	.	6.46	5.44	7.98	7.86	
	.795	4.51	4.18	5.70	5.51	
	.227	2.41	2.26	3.02	2.97	

The following table gives the currents with $\frac{1}{10}$ normal solution of chlorides and nitrates:—

E.M.F.	Chlorides			Nitrates		
	5.60	.795	.227	5.60	.795	.227
Cæsium . .	123	60.5	22.2	303	115	36.6
Rubidium . .	11.4	26.4	11.3	213	82.4	25.9
Potassium . .	21.0	13.4	5.75	68.4	29.3	9.35
Sodium . .	3.40	2.45	1.15	3.88	2.67	1.32
Lithium . .	1.29	.87	.41	1.47	.99	.53
Hydrogen . .	.75		.27			

As already mentioned, Arrhenius suggested that since all salts of any one metal give equal currents, they are all converted into hydroxides by the water vapour in the flame. On this view, the later experiments indicate that at the higher concentrations the conversion into hydroxides is not complete.

The conductivity of salt vapours in a current of air was measured by the writer in 1901¹. The apparatus used is shown in Fig. 25

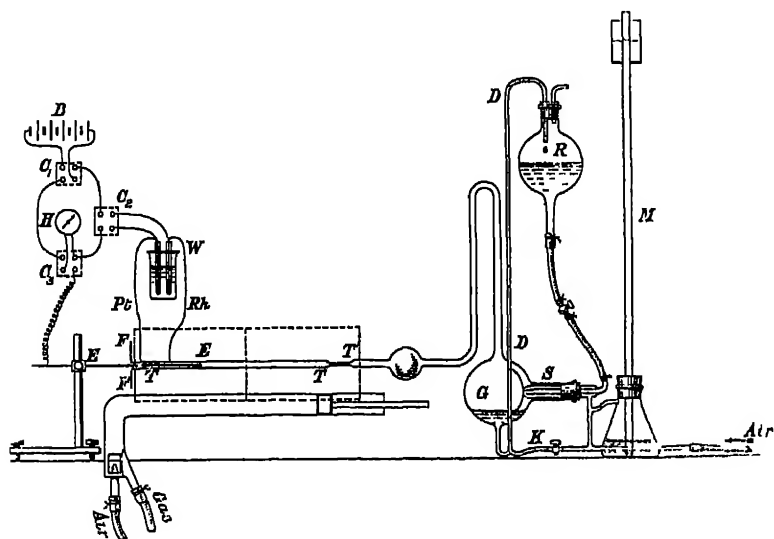


FIG 25

It consisted of a platinum tube TT, 37 cms. long and 0.75 cm. in diameter, having a narrow tube T' joined at one end, and a flange FF, 6 cms in diameter, joined on at the other. This tube was supported horizontally in a Fletcher's tube furnace, the fire-clay blocks of which are shown by the dotted lines. The flange served to keep the furnace gases from the open end of the tube. An electrode, EE, consisting of a platinum tube, 12 cms long and 0.3 cm. in diameter, was supported on an adjustable insulated stand, along the axis of the tube TT. The end of this electrode

¹ *Phil. Trans. A.* vol. 197, p. 415, 1901. *Phil. Mag.*, August 1902.

was closed by a conical platinum cap, which was about 9 cm down the tube TT.

At T' the platinum tube was sealed on to a glass tube, through which the air charged with spray entered. The spray was produced by a Gouy sprayer, S, which projected the spray into glass bulb, G, about 8 cms in diameter, from which the air and spray were led through an inverted U-tube, in which the coarse spray settled.

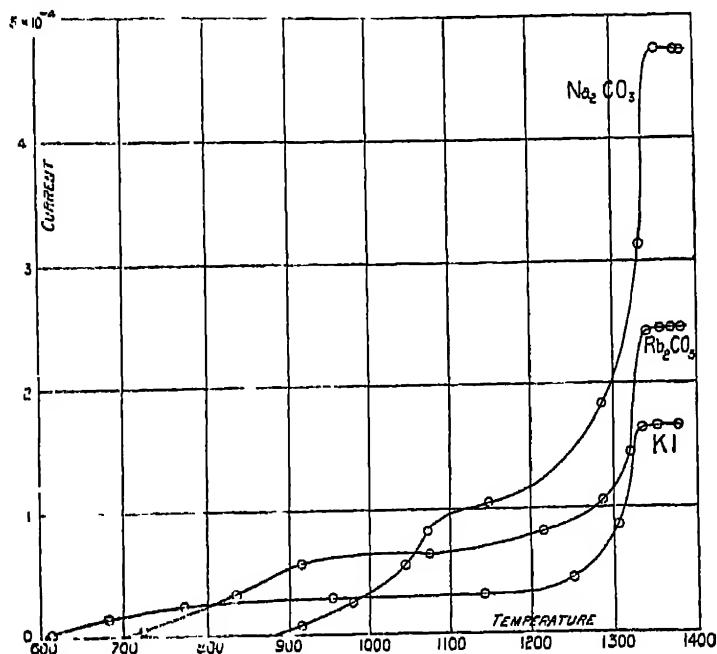


FIG. 20

The salt solution was contained in a reservoir R, the level of the surface of the solution being 30 cms. above the nozzle of the sprayer. The greater part of the spray settled in the bulb at the first half of the U-tube, and was returned to R through a tube DD, up which the liquid was forced by air introduced by the tube R. The supply of compressed air used was obtained by means of two water injector pumps. The air pressure at the sprayer was measured by means of the water manometer M.

The temperature of the tube was measured by means of a platinum platinum-rhodium thermocouple.

The following table gives the currents observed with a one per cent solution of caesium chloride at 1340° C. —

P D volts.	Current (amperes)	
	Outer tube —	Inner tube —
1200	8.8×10^{-4}	15.1×10^{-4}
800	8.7 "	13.1 "
600	8.8 "	9.3 "
400	7.6 "	4.3 "
200	2.3 "	1.1 "
120	0.9 "	0.5 "
40	0.2 "	0.1 "

These results are typical of the behaviour of most alkali salts.

Fig 26 shows the variation of the current with the temperature in several cases.

It was found that above 800 volts the current was nearly saturated in nearly all cases, and also that above 1400° C. the current was nearly independent of the temperature. It appeared, therefore, that there was a maximum possible current which could not be increased by raising either the P.D. or the temperature.

The table on p 97 gives the values found for this maximum possible current.

It is clear that the maximum current is proportional to the strength of the solution sprayed, and inversely proportional to the electro-chemical equivalent of the salt.

Let M denote the mass of salt entering the tube per sec. and Q the total charge on all the positive or negative ions formed from this amount of salt. Then it appears from the above results that

$$\frac{Q}{M} = \frac{A}{E}$$

where A is a constant and E denotes the electro-chemical equivalent of the salt.

According to Faraday's laws of electrolysis, one gram-equivalent of any salt in the liquid state is electrolysed by the passage of 96,440 coulombs, or

$$\frac{Q}{M} = \frac{96,440}{E}$$

Salt	Grams per litre	Electro- chemical Equivalent, M	Current C	EC
CsCl	10	168	15.1×10^{-4}	2.54×10^{-1}
RbI . .	10	212	13.5 "	2.86 "
KI	10	166	16.4 "	2.72 "
NaI . .	10	150	16.4 "	2.46 "
CsCl	1	168	1.61 "	2.70×10^{-2}
Cs ₂ CO ₃ .	1	163	1.61 "	2.62 "
RbI	1	212	1.25 "	2.65 "
RbCl	1	121	2.24 "	2.71 "
Rb ₂ CO ₃ .	1	115	2.44 "	2.80 "
KI	1	166	1.66 "	2.75 "
KBr . . .	1	119	2.13 "	2.53 "
KF . . .	1	58	4.42 "	2.57 "
K ₂ CO ₃ . .	1	69	4.00 "	2.76 "
NaI . . .	1	150	1.82 "	2.73 "
NaBr . . .	1	103	2.44 "	2.52 "
NaCl . . .	1	59	4.73 "	2.79 "
Na ₂ CO ₃ . .	1	53	4.73 "	2.51 "
LiI . . .	1	134	2.03 "	2.72 "
LiBr . . .	1	87	3.12 "	2.72 "
LiCl . . .	1	43	6.25 "	2.69 "
Li ₂ CO ₃ . .	1	37	7.48 "	2.77 "

where Q is the quantity of electricity required to electrolyse a mass M of the salt.

The amount of salt entering the tube was estimated by burning the air and spray along with coal gas, so as to give a Bunsen flame. An equal flame was arranged near the first one, in which a bead of salt on a platinum wire could be placed. By adjusting the position of the bead it was possible to arrange so that the two flames were equally brightly coloured by the salt. The loss of weight of the bead in a known time then gave the amount of salt passing through the tube. This method was first used by Arrhenius.¹ In this way it was found that when a solution containing one gram per litre was sprayed, 2.7×10^{-7} grams of salt entered the tube per second.

¹ *Wied. Ann.* vol. xlii. p. 18, 1891.

Hence we get

$$A = \frac{EQ}{M} = \frac{2\,63 \times 10^{-2}}{2\,70 \times 10^{-7}} = 98,600 \text{ coulombs.}$$

This agrees as well as could be expected with the value 96,440 found for solutions. It appears, therefore, that Faraday's laws of electrolysis of liquids apply also to salts in the state of vapour. In other words, Q/M is the same in salt vapours at 1400°C as in solutions at the ordinary temperature

Since equivalent weights of the alkali salts contain equal numbers of metal atoms, it follows that the charge carried by the salt vapours per atom of metal is the same as the charge on one monovalent ion in solutions

The ratio of the charge e to the mass m for the positive ions of alkali sulphates has recently been determined by O. W. Richardson,¹ by observing their deflection in a magnetic field. The method used was the same as that described in Chap. V for the positive ions emitted by a hot strip of platinum. The hot strip was coated with the alkali sulphate. The following table gives the mean values of e/m found by Richardson

Since in the electrolysis of solutions one gram of hydrogen is deposited by the passage of 9644 electromagnetic units of electricity, we have e/m for a hydrogen atom in solutions equal to 9644. If we divide 9644 by the values of e/m found for the positive ions, we get their equivalent weights

Substance.	e/m	Equivalent weights of + ions (H = 1)	Atomic weights of metals.
Li_2SO_4	1600	6.0	7.0
Na_2SO_4	430	22.5	23.1
K_2SO_4	265	36.4	39.2
Rb_2SO_4	101	96	85.4
Cs_2SO_4	73	132	133

It is clear from these results that the positive ions emitted by the alkali sulphates at high temperatures contain the metal only,

¹ *Phil. Mag.*, December 1910.

and that the charge per atom of metal is the same as in solutions. These experiments, however, give no information as to the number of atoms of the metal in each ion. As we have seen, the positive ions in flames are probably single atoms, so that most likely the same is true in the present case. Davisson¹ has made a series of measurements of e/m for the positive ions emitted by salts of the alkaline earths. He found they were single atoms of the metal with single ionic charges in most cases.

APPENDIX

Since all alkali salts give positive ions having equal apparent velocities, Langevin² suggested that these ions consist of hydrogen atoms. The formula $h = e\lambda/mv$ gives about 300 for a hydrogen atom in a flame at 2000° C. This view is supported by Lusby (*loc. cit.*), who finds $h = 300$. I think Lusby's value is too high and prefer the explanation of the equality of the velocities given above. However, the question must be regarded as an open one, and further experiments are required before a definite conclusion can be arrived at.

¹ *Phil. Mag.*, January 1912

² *Comptes rendus*, t. CXL., 1905, p. 35.



CHAPTER VIII

THE ELECTRICAL CONDUCTIVITY OF FLAMES FOR RAPIDLY ALTERNATING CURRENTS

THE conductivity of flames for rapidly alternating currents was investigated by E. Gold and the writer.¹ The apparatus used is shown in Fig 27.

A mixture of coal gas and air containing spray was burnt as a non-luminous flame, with a sharply defined inner cone. The

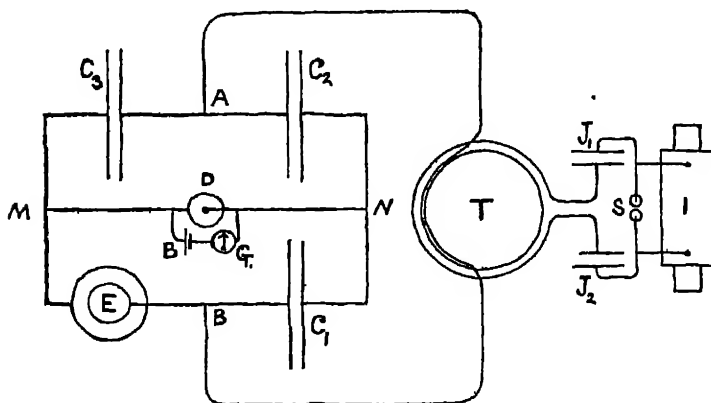


FIG 27.

electrodes used were concentric platinum cylinders 5 cms. high and 2.4 and 1.2 cms. in diameter.

The conductivity between the electrodes was determined by means of a Wheatstone-bridge arrangement, of which the electrodes formed one arm, and the other three arms consisted of small air condensers, the capacity of one of which was adjustable with a micrometer screw.

An induction-coil, I, charged two Leyden jars J_1 , J_2 , and these

¹ *Phil Mag.*, April 1906

discharged at a spark gap S. The outside coatings of the jars were connected through the primary of a Tesla coil, T. The primary of this coil consisted of 33 turns wound into a spiral, 29 cms. long and 19 cms. in diameter, on a glass cylinder. The secondary coil had three turns, and was placed inside the glass cylinder, half-way up it. It was connected to the bridge arrangement at A and B, as shown.

An "electrolytic detector," D, was connected to the points M and N of the bridge. This detector consisted of two platinum electrodes dipping into 20 per cent. sulphuric acid. One electrode was a platinum cylinder 3 cms. in diameter and 4 cms. high, while the other was a platinum wire $\frac{1}{1000}$ inch in diameter sealed into a glass tube and cut off close to the surface of the glass. The two electrodes were connected to a silver-chloride cell B and a galvanometer G. The cell B gave about one volt, and served to polarize the electrodes. When an alternating P.D. was produced between M and N the detector was depolarized and a current passed through the galvanometer. The condensers C_1 and C_2 each consisted of two parallel circular discs, 10 cms. in diameter, well insulated. The distance between the discs of C_1 was 0.15 cm., and of C_2 0.75 cm., in most of the experiments. The condenser C_3 consisted of two discs, 10 cms. in diameter, whose distance apart could be adjusted and measured with a micrometer screw.

On working the coil with the electrodes E in the flame, it was found that by adjusting the capacity of the condenser C_3 the galvanometer deflection could be reduced to a very small minimum value. This shows that the electrodes in the flame for very rapidly alternating currents behave like a capacity or a self-induction, and not like a resistance.

The change in the capacity of a parallel plate condenser is very nearly proportional to the change in the reciprocal of the distance between its plates. Thus, if d_2 is the distance with which the bridge is balanced with a flame filled with salt, and d_1 that for the flame free from salt, the $d_2^{-1} - d_1^{-1}$ is proportional to the change in the apparent capacity of the flame electrodes due to introducing the salt.

It was found that $d_2^{-1} - d_1^{-1}$ was approximately independent of

number per sec was changed from 7×10^4 to 6×10^6 , $d_2^{-1} - d_1^{-1}$ changed from 2.1 to 3.0. If we suppose the change in $d_2^{-1} - d_1^{-1}$ proportional to n^x , where n is the number of alternations per sec., then this shows that x is not greater than 0.05. For a pure capacity $x = 0$, and for a pure self-induction $x = 1$, so that it appears that the flame behaves nearly like a pure capacity.

The variation of $d_2^{-1} - d_1^{-1}$ with the P D at constant frequency was examined, and it was found to be nearly inversely proportional to the square root of the P D.

With parallel plate electrodes, $d_2^{-1} - d_1^{-1}$ was nearly independent of the distance between the electrodes.

THEORY OF THE CONDUCTIVITY FOR RAPIDLY ALTERNATING CURRENTS.

Suppose a large parallel plate condenser filled with a uniformly ionized gas, and let the distance between the plates be D cms. Let the potential difference between the plates be given by the formula $V = V_0 \sin pt$, and let the number of positive or negative ions per c.c. be n , each ion carrying a charge $\pm e$. In a Bunsen flame, the velocity of the negative ions is about one hundred times that of the positive ions, and the mass of the positive ions is very large compared with that of the negative ions, so that in a rapidly alternating electric field the amplitude of vibration of the negative ions must be very large compared with that of the positive ions.

For an approximate calculation, therefore, we may assume that the positive ions do not move, so that all the current is carried by the negative ions. Also, let us suppose that all the negative ions move in the same way, with the same velocity, so that the number of negative per c.c. remains n except within a distance d of each electrode, d being twice the amplitude of vibration of the negative ions. It is easy to see that on these assumptions the negative ions will practically all be contained in a slab of thickness $D - d$, which will vibrate between the plates so as just not to touch either of them. For if a new negative ion is formed outside the slab it will almost immediately strike the electrode near it; whereas a new negative ion formed in the slab cannot reach either electrode,

except by diffusion, which we shall neglect. Thus we may regard the whole space between the plates as filled with positive electricity of density $+ne$, and the vibrating slab of thickness $D - d$ as containing also negative electricity of density $-ne$. Thus inside the slab the total density is zero, and outside is $+ne$.

Let X denote the electric intensity between the plates at a distance x from one of them. Then, inside the slab $\frac{dX}{dx} = 0$, and outside $\frac{dX}{dx} = 4\pi ne$

Let A and B (Fig. 28) be the two plates, and let the slab be represented by the space between the two dotted lines E, F. Let

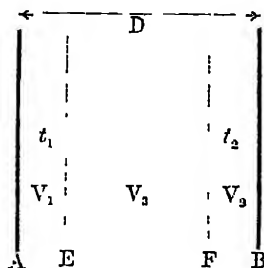


FIG. 28.

$AB = D$, $AE = t_1$, $FB = t_2$, and suppose the potential of A kept zero, while that of B $= V$. Let the rise of potential in AE be V_1 , in EF be V_2 , and in FB be V_3 . In EF let $X = X_0$. Then $V_3 = -X_0(D-d)$, where $d = t_1 + t_2$. In AE we have $\frac{d^2V}{dx^2} =$

$-4\pi\rho$, where $\rho = ne$. From this we get $\frac{dV}{dx} = -4\pi\rho x + C$

and $V = -2\pi\rho x^2 + Cx + D$, where C and D are constants to be determined. When $x = 0$, $V = D = 0$, and when $x = t_1$ —

$$\frac{dV}{dx} = -4\pi\rho t_1 + C = X_0$$

Hence—

$$V_1 = 2\pi\rho t_1^2 - X_0 t_1.$$

In the same way in FB we have

$$V = -2\pi\rho x^2 + C'x + D'$$

When $x = D - t_2$ $\frac{dV}{dx} = -X_0$ and $V = V_1 + V_3$,

so that we get for V at $x = D$ —

$$V = -X_0 D + 2\pi\rho(t_1^2 - t_2^2).$$

Now $t_1 + t_2 = d$, so that

$$V = -X_0 D + 2\pi\rho d(2t_1 - d) \quad \dots \quad (1)$$

The force acting on a negative ion is $-X_0 e - A \frac{dt_1}{dt}$, where A is a constant representing the viscous resistance to motion with unit velocity. Let m be the mass of a negative ion; then its equation of motion is

$$-X_0 e = m \frac{d^2 t_1}{dt^2} + A \frac{dt_1}{dt} \quad \dots \quad (2)$$

The current density inside the slab is given by the equation—

$$i = -\rho \frac{dt_1}{dt} + \frac{K}{4\pi} \frac{dX_0}{dt}$$

where K is the specific inductive capacity of the medium between the plates in the absence of ions. Thus, K is unity, and

$$i = -\rho \frac{dt_1}{dt} + \frac{1}{4\pi} \frac{dX_0}{dt} \quad \dots \quad (3)$$

Now, in a flame containing a salt vapour, the fall of potential nearly all takes place near the electrodes, so that X_0 is probably very small, even when rapidly alternating currents are used. Consequently, since ρ is large, $\frac{1}{4\pi} \frac{dX_0}{dt}$ may be neglected in comparison with $-\rho \frac{dt_1}{dt}$. Hence (3) becomes $i = -\rho \frac{dt_1}{dt}$ approximately.

Substituting in (1) the value of X_0 got from (2), we get

$$V = V_0 \sin pt = D \left(\frac{m}{e} \frac{d^2 t_1}{dt^2} + \frac{A}{e} \frac{dt_1}{dt} \right) + 2\pi\rho d(2t_1 - d).$$

This gives

$$V_0 p \cos pt = \frac{mD}{e} \frac{d^2 t_1}{dt^2} + \frac{AD}{e} \frac{dt_1}{dt} + 4\pi\rho d \frac{dt_1}{dt}.$$

But $\frac{dt_1}{dt} = -\frac{i}{\rho}$. Hence—

$$-V_0 p \cos pt = \frac{mD}{e\rho} \frac{d^2 i}{dt^2} + \frac{AD}{e\rho} \frac{di}{dt} + 4\pi i d \quad \dots \quad (4)$$

The solution of this equation is

$$i = \frac{-\frac{e\rho}{mD} V_0 \sin(pt - \alpha)}{\left\{ \left(1 - \frac{4\pi d e \rho}{p^2 m D}\right)^2 p^2 + \frac{A^2}{m^2} \right\}^{\frac{1}{2}}} \quad \dots \quad (6)$$

where

$$\tan \alpha = \frac{-\left(1 - \frac{4\pi d e \rho}{p^2 m D}\right) p m}{A}$$

If a P.D. $V = V_0 \sin pt$ is applied to a condenser of capacity C the current is given by the equation $i = CV_0 p \cos pt$. For the flame, if A and m are both negligible, (5) becomes

$$i = -\frac{V_0 p \cos pt}{4\pi d}$$

so that the apparent capacity is $\frac{1}{4\pi d}$ per unit area. Now $\frac{d}{2}$ is the amplitude of vibration of the negative ions, so that ρd must be the amount of electricity flowing during a half vibration.

Let $i = -\frac{dQ}{dt}$, so that $Q = \frac{V_0}{4\pi d} \sin pt$. Then we have, integrating from 0 to π ,

$$\rho d = \frac{V_0}{2\pi d} \text{ or } d = \sqrt{\frac{V_0}{2\pi\rho}}$$

so that the apparent capacity per unit area is

$$\frac{1}{4\pi d} = \sqrt{\frac{\rho}{8\pi V_0}}.$$

If $\rho = 0$ this makes the capacity zero, whereas it should be $\frac{1}{4\pi D}$. This is due to the omission of $\frac{1}{4\pi} \frac{dX_0}{dt}$, which would not be negligible if ρ were small. If, however, we take $\sqrt{\frac{\rho}{8\pi V_0}}$ to be the increase in the apparent capacity due to the presence of the ions, then no error will be made, even if ρ be small.

According to the theory, therefore, we should expect the apparent capacity to be independent of the number of alternations per second, and of the distance between the electrodes, and to be inversely proportional to the square root of the potential difference

between the electrodes, which agrees exactly with the experimental results.

The expression $\sqrt{\frac{q}{8\pi V_0}}$ has been obtained by neglecting the mass of the negative ions, and the resistance to their motion, so that it appears that the alternating current through the flame is determined merely by the density of the layer of positive charge left in the gas near the electrodes when the negative ions move under the action of the alternating electric field.

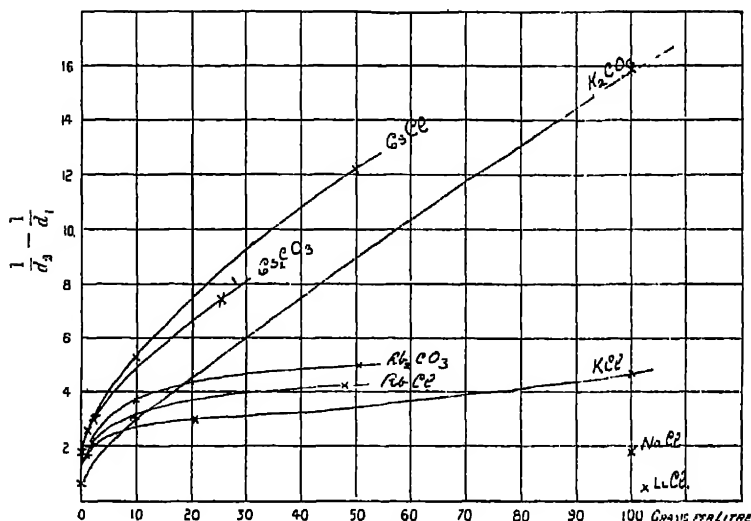


FIG 29

If a steady P.D. is applied to two electrodes immersed in an ionized gas, and if the positive ions cannot move, it is easy to see that a current will only pass for the short time required for the accumulation of a positive charge near the negative electrode to become sufficient to make the electric force near the positive electrode zero. Thus the two electrodes will behave like a condenser when the P.D. is applied. When a rapidly alternating P.D. is applied it is easy to see that even if the positive ions move, provided their velocity is small compared with that of the negative ions, the arrangement will behave like a condenser if the number of ions per c.c. is very large, and the mass of the negative ions very small.

ELECTRICAL CONDUCTIVITY OF FLAMES 1

The following table gives the values found for $d_2^{-1} - d_1^{-1}$ with a number of salt solutions sprayed into the flame.—

Salt	Grams per litre	d_2 (in tenths of an inch)	$\frac{1}{d_2} - \frac{1}{d_1}$
CsCl	50	0.08	12.2
"	10	0.18	5.26
"	1	0.34	2.64
"	0.333	0.48	1.78
"	0.1	1.10	0.61
Cs ₂ CO ₃	25.5	0.13	7.40
"	2.55	0.30	3.03
"	0.26	0.59	1.40
"	0.026	1.90	0.23
RbCl	48.1	0.22	4.24
"	9.6	0.29	3.15
"	1.92	0.41	2.14
Rb ₂ CO ₃	50.4	0.19	4.96
"	10	0.25	3.70
"	1	0.50	1.70
K ₂ CO ₃	100	0.062	15.8
"	10	0.297	3.07
KCl	100	0.20	4.70
"	20.8	0.30	3.03
"	1	0.50	1.70
NaCl	100	0.47	1.83
LiCl	102.5	1.3	0.47

In Fig. 29 the above values of $d_2^{-1} - d_1^{-1}$ are shown graphically. Fig. 30 shows the steady currents due to an E.M.F. of 0.227 v. between cylindrical electrodes in a flame, taken from the paper Smithells, Dawson and the writer (see p. 92).

The amount of salt entering the flame per second was nearly the same in the two sets of experiments.

The following table gives the values of $d_2^{-1} - d_1^{-1}$ for decinormal solutions obtained from the curves in Fig. 29, and also the steady currents due to 0.227 volt.—

Salt	$\frac{1}{d_2} - \frac{1}{d_1}$ (k)	Salt	Steady Current ($1=10^{-7}$ ampere) (k')	Ratios	\sqrt{k} k
CsCl . .	6.7	CsCl . .	22.2	3.3	0.70
$\frac{1}{2}$ Cs ₂ CO ₃	5.9	CsNO ₃	36.6	6.2	1.03
$\frac{1}{2}$ Rb ₂ CO ₃	3.7	RbNO ₃ .	25.9	7	1.37
RbCl . .	3.2	RbCl . .	11.3	3.5	1.05
$\frac{1}{2}$ K ₂ CO ₃ .	2.9	$\frac{1}{2}$ K ₂ CO ₃ .	11.2	3.9	1.15
KCl . .	2.6	KCl . .	5.75	2.2	0.92

In the work with steady currents the conductivities of caesium and rubidium carbonates were not measured, so the values for nitrates are given, since the conductivities of all oxysalts of the same metal were found to be nearly equal for steady currents.

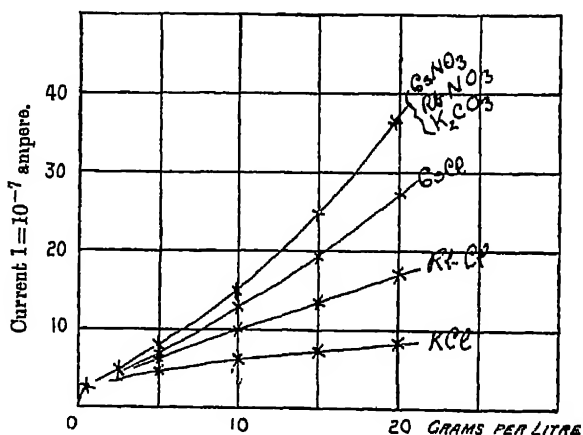


FIG 80

The last column contains the square root of the conductivity for steady currents divided by $d_2^{-1} - d_1^{-1}$. The numbers in this column do not vary much, which shows that the conductivity for rapidly alternating currents varies nearly as the square root of the conductivity for steady currents.

The conductivities of potassium chloride and rubidium chloride were found to vary nearly as the square root of the concentration

for steady currents; so that we should expect them to vary as the fourth root of the concentration for rapidly alternating currents and this was found to be approximately true¹

The steady currents due to 0.227 volt are probably proportional to the number of ions present per c.c. in the flame, so that the comparison of the conductivities for steady and alternating P.D.'s shows that for the latter the conductivities as measured by $d_2^{-1} - d_1^{-1}$ are proportional to the square root of the number of ions present per c.c. This is what we should expect from the formula $\sqrt{\frac{e}{8\pi V_0}}$, for $e = ne$.

It appears, therefore, that the theory considered agrees very well with the facts.

If c denotes the increase in the apparent capacity per unit area, we have

$$c = \sqrt{\frac{e}{8\pi V_0}} = \frac{K-1}{4\pi D}$$

where K is the apparent specific inductive capacity of the salt vapour. Hence $e = \frac{V_0(K-1)^2}{2\pi D^2}$. With air between the electrodes instead of flame, d was equal to 0.66, while with the flame free from salt, it was 3.33. Hence $K = \frac{6.66}{d_2}$ very nearly.

The table on p. 110 gives a few values of K . K , of course, has no relation to the true specific inductive capacity of the salt vapours, which must be little different from unity. The third column contains the values of the number of ions per c.c. given by the equation $ne = \frac{V_0(K-1)^2}{2\pi D^2}$. V_0 was about 1.2 E.S. units, and D was 0.6 cm. e was taken to be 5×10^{-10} E.S. units, so that $n = 1.06 \times 10^9(K-1)^2$.

The amount of salt entering the flame per minute when a solution containing one gram per litre was sprayed was 0.053 milligram. The velocity of the flame gases was about 200 cms. per sec., and the diameter of the flame about 3 cms., so that the

¹ H. A. Wilson and E. Gold (*loc. cit.*).

Salt.	Grams per litre.	K	n	N
Cs_2CO_3	25.5	51	2.7×10^{12}	5.5×10^{11}
"	2.55	22	4.7×10^{11}	5.5×10^{12}
"	0.26	11	1.1×10^{11}	5.6×10^{11}
"	0.026	3.5	6.7×10^9	5.6×10^{10}
CsCl	50	83	7.2×10^{12}	10^{11}
"	10	37	1.4×10^{12}	2×10^{11}
"	1	20	3.9×10^{11}	2×10^{12}
"	0.1	6	2.7×10^{10}	2×10^{11}
RbCl	48.1	30	9×10^{11}	1.4×10^{14}
"	1.92	16	2.4×10^{11}	5.6×10^{12}
K_2CO_3	100	107	1.3×10^{13}	5.1×10^{14}
"	10	22	4.7×10^{11}	5.1×10^{13}
KCl	100	33	1.1×10^{12}	4.7×10^{14}
"	20.8	22	4.7×10^{11}	9.7×10^{13}
"	1	12	1.3×10^{11}	4.7×10^{12}
NaCl	100	14	1.8×10^{11}	5.9×10^{14}
LiCl	102.5	5	1.7×10^{10}	8.4×10^{11}
Free flame	—	2	1.1×10^9	

mount of salt per c.c. in the flame was about $G \times 6 \times 10^{-7}$ milligram with a solution containing G grams per litre

Let N denote the number of metal atoms per c.c., and E the chemical equivalent of the salt. Then

$$N = \frac{G \times 9644 \times 3 \times 10^{10} \times 6 \times 10^{-10}}{5 \times 10^{-10} \times E} = \frac{G}{E} \times 3.5 \times 10^{14}$$

$r \frac{9644}{eE}$ is the number of metal atoms in one gram of the salt. The last column in the above table contains the values of N given by this formula.

It will be seen that with the dilute solutions of caesium salts the number of ions is about one-tenth the number of metal atoms present. With salts of the other metals the proportion of ions is less. The values of n and N , of course, are subject to a large possible error. For caesium salts at very small concentrations it seems probable that n and N do not really differ very much.

We can get a rough estimate of the velocity of the negative ions¹ in the flame without salt by using the value of $n (= 1.1 \times 10^9)$ and the known conductivity of the flame for steady currents. We

¹ E. Gold, *Proc. Roy. Soc. A.* vol. 79, p. 43, 1907

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have $\iota = Xne(k_1 + k_2)$ and $\frac{\iota}{X} = 10^{-15}$ E.M. units,¹ $e = 1.7 \times 10^{-19}$

Hence $k_1 + k_2 = 5.3 \times 10^{-6}$. But k_1 is small compared with so that for one volt per cm. we get $k_2 = 5300$. This agrees well as could be expected with the theoretical value for a negative electron

¹ See p. 62

CHAPTER IX

FLAMES IN A MAGNETIC FIELD

It will be convenient to begin by considering the theory of the effect of a magnetic field on a flame. Suppose that a thin plane vertical sheet of flame moving upwards with velocity V is acted on by a magnetic force of strength H perpendicular to the sheet. Let there be a vertical uniform electric field of strength Y upwards in the flame.

Since the velocity of the negative ions is very large compared with that of the positive ions, only the former need be considered. The equations of motion of a negative ion describing a free path are

$$\begin{aligned} m \frac{d^2x}{dt^2} &= Xe - He \frac{dy}{dt} \\ m \frac{d^2y}{dt^2} &= Ye + He \frac{dx}{dt} \\ m \frac{d^2z}{dt^2} &= 0 \end{aligned}$$

where y is measured vertically upwards, and x horizontally at right angles to the magnetic field.

If we regard the gas as a viscous medium, exerting a force on the ions proportional to their velocity, the equations of motion become

$$\begin{aligned} m \frac{d^2x}{dt^2} &= Xe - He \frac{dy}{dt} - \frac{e}{k'_2} \frac{dx}{dt} \\ m \frac{d^2y}{dt^2} &= Ye + He \frac{dx}{dt} - \frac{e}{k'_2} \left(\frac{dy}{dt} - V \right) \\ m \frac{d^2z}{dt^2} &= - \frac{e}{k'_2} \frac{dz}{dt} \end{aligned}$$

here k'_2 is the value of k_2 in the magnetic field, and differs slightly from k_2 .

In a steady state, therefore, putting $u = \frac{dx}{dt}$, $v = \frac{dy}{dt}$, we get

$$X = Hv + \frac{u}{k_2'}$$

$$Y = -Hu + \frac{v - V}{k_2'}$$

If the sides of the flame are insulated the velocity u must be zero, since there can be no horizontal current; so that

$$X = Hv$$

$$Y = \frac{v - V}{k_2'}$$

which give $X - HV = k_2' YH$.

If the top and bottom of the flame are insulated the upward velocity of the negative ions must be equal to that of the positive ions, which move with the flame, so that—

$$X = HV + \frac{u}{k_2'}$$

$$Y = -Hu,$$

which give $Y = -k_2' H(X - HV)$

If Y is one volt per cm, or 10^8 , $k_2' YH$ is about 10^4 ; so that V which is about $200 \frac{\text{cm}}{\text{sec}}$, can be neglected compared with $k_2' Y$

In the above I have assumed that X and Y are uniform. The transverse stream of negative ions requires an excess of ionization over recombination along one side of the flame, and an equal excess of recombination along the other. Consequently, near the edges X and Y will not be uniform, but a little way from the edges the ionization and recombination will be equal, and X and Y uniform. In measuring X or Y it is, consequently, necessary to measure the P.D. between wires put in a little way from the edges of the flame. Near the electrodes used to produce the field it will not be uniform, so that these electrodes ought to be some distance from the place where the transverse field is measured.

The condition that the sides of the flame be insulated is difficult to fulfil in practice. For example, if a small flat flame is placed between the poles of a magnet so that the top and

bottom of the flame are in a weaker field than the middle, the charges corresponding to the induced field X can leak across the top and bottom of the flame. In consequence, the actual value of X will be less than that calculated. If horizontal electrodes are put in the flame they connect together the sides, and so must greatly diminish X . To get the full theoretical value of X it is necessary that the length of flame in the magnetic field should be large compared with the breadth of the flame, and also that the horizontal electrodes should be a long way from the place where X is measured. These conditions have to be satisfied in measuring the Hall effect in a thin metal plate, as is well known.

The Hall effect in Bunsen flames has been examined by E. Marx¹ He used a small flat flame between the poles of a magnet. The electrodes were horizontal gratings, through which the flame passed. Unfortunately these electrodes seem to have only been two or three cms apart, while the breadth of the flame was also about two or three cms. Consequently, the sides of the flame were really connected together by the electrodes, instead of being insulated. Consequently the values found for the transverse electric force must be much smaller than the theoretical value.

The horizontal electric field X was measured by two wires connected to a quadrant electrometer.

The following table gives some of the value found for X/HY with potassium chloride solutions sprayed into the flame:—

Concentration of Solution	X/HY
0	$- 10.18 \times 10^{-6}$
0.125 normal	- 8.24 "
0.5 "	- 4.26 "
2.0 "	- 3.78 "
3.8 "	- 3.75 "

For strong solutions X/HY was nearly independent of the concentration.

¹ *Ann. der Physik*, Band 2, 1900.

The following table gives the values found with strong solution of salts of all the alkali metals :—

Metal	X/HY
Caesium .	$- 1.72 \times 10^{-6}$
Rubidium .	$- 2.7$ "
Potassium	$- 3.72$ "
Sodium .	$- 5.06$ "
Lithium	$- 7.86$ "

These numbers are nearly inversely proportional to the square roots of the atomic weights of the metals.

We have $k_2' = \frac{X}{HV} \times 10^8$ for one volt per cm. approximately

for HV is small compared with X. Marx's results, therefore, indicate values of k_2' varying from 1018 for the flame without salt, down to 172 for caesium salts. If the negative ions are free electrons, which is probable, k_2' ought to be about 20,000. The short-circuiting of the sides of the flame by the horizontal electrode probably explains the low values found for X/HY and the variation of it. The values found are lower the greater the conductivity of the flame, which is what we might expect. Consequently, these experiments do little more than indicate that the Hall effect exists, and is in the direction to be expected from the fact that k_2 is much greater than k_1 .

Some measurements of the Hall effect made under my direction a few years ago, but not hitherto published, indicated a value of X/YH about ten times that found by Marx for the flame free from salt. In these experiments care was taken to have the horizontal electrodes sufficiently far from the place where X was measured. These experiments gave k_2 equal to about 10,000, which is of the order of magnitude to be expected for free electrons.

The effect of a magnetic field on the conductivity of the Bunsen flame was examined by the writer.¹ The flame used consisted of a row of twelve small Bunsen flames, burning from quartz tubes

¹ *Proc. Roy. Soc. A.* vol. 82, 1909.

These gave a flame about 14 cms. long, 6 cms high, and 2 cms. thick

A current was passed horizontally along the flame between two platinum electrodes, and the uniform potential gradient between the electrodes was measured by means of two exploring wires 7 cms apart, connected to an electrostatic voltmeter

The flame was placed between the poles of a large electro-

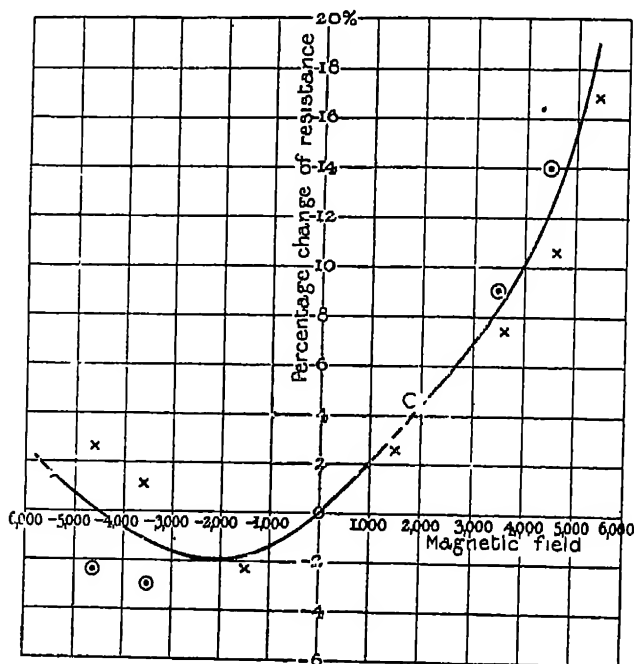


FIG 31

magnet, which gave a nearly uniform field over the entire area of the flame between the exploring wires.

Some potassium carbonate was put on the negative electrode to diminish the drop of potential there, and so increase the current. There was no salt in the part of the flame between the poles of the magnet. The ratio of the potential difference between the exploring wires to the current was taken as a measure of the resistance of the flame

Fig 31 shows the results obtained

The curve drawn is that given by the equation—

$$100 \frac{dR}{R} = 3.1 \times 10^{-7} H^2 + 1.5 \times 10^{-8} H$$

ere R denotes the resistance and H the magnetic field. It appears, therefore, that the effect of the magnetic field is made of two parts, one proportional to the square of the field, and another proportional to the field. The lack of symmetry is evidently connected with the upward motion of the flame.

We have seen that when the top and bottom of the flame insulated the horizontal velocity of the negative ions is given by $u = k_2' (X - HV)$, so that the conductivity is given by $= ne k_2' \left(1 - \frac{HV}{X}\right)$, where C denotes the current.

In the absence of a magnetic field the current C_0 is given by

$$C_0 = ne k_2 X_0$$

Putting $\sigma_0 = C_0/X_0$, $\sigma = C/X$, $k_2' - k_2 = \delta k_2$, and $\sigma - \sigma_0 = \delta\sigma$, obtain, approximately,

$$\frac{\delta\sigma}{\sigma} = \frac{\delta k_2}{k_2} - \frac{HV}{X}$$

We have $k_2 = 1.4 \frac{e\lambda}{m\bar{U}}$, so that to get the change in k_2 it is necessary to calculate the change in λ , the mean free path, due to magnetic field. Consider a particular free path making an angle θ with H . There are three forces acting on the electron—

- (1) Xe
- (2) $Ye = -ek_2H(X - HV)$
- (3) $HeU \sin \theta$.

The electric force X was about 10 volts per cm., or 10^9 , X was therefore about 10^8 , while HU is about 10^{10} , since $= 3 \times 10^7$. Consequently, the force Ye can be neglected, so the effect of the magnetic field is due to the force $HeU \sin \theta$. This force causes the electron to describe an arc of a circle of radius ρ given by

$$\frac{mU^2}{\rho} = HeU \sin \theta.$$

If l is the length of the straight line between the ends of the path, and l' the length along the arc, we have, therefore,

, , ,

Hence, since $\frac{l'}{2Q}$ is small,

$$\frac{l' - l}{l'} = \frac{l'^2}{24Q^2} = \frac{l^2 H^2 c^2 \sin^2 \theta}{24m^2 U^2}.$$

The mean value of $\sin^2 \theta$ is $\frac{2}{3}$, that of l^2 is $2\lambda^2$, and that of U^{-2} is $3\bar{U}^{-2}$, so that the mean value of $(l' - l)/l'$ is equal to $\frac{1}{3} \frac{H^2 c^2 \lambda^2}{m^2 \bar{U}^2}$.

Hence, since $\frac{2e^2 \lambda^2}{m^2 \bar{U}^2} = k_2^2$,

$$\frac{\delta k_2}{k_2} = -\frac{1}{12} H^2 k_2^2$$

for the time of describing the free paths is increased in the ratio of l' to l .

Sir J. J. Thomson, who first calculated the effect of a magnetic field on conductivity, on the electron theory, got $\frac{1}{3} H^2 k_2^2$, but he did not take into account the variations of λ and U .

The equation which was found to represent the experimental results was—

$$\frac{\delta R}{R} = 3.1 \times 10^{-9} H^2 + 1.5 \times 10^{-5} H$$

If we assume that the term in H^2 is equal to $\frac{1}{12} H^2 k_2^2$ we get $k_2 = 1.8 \times 10^{-4}$ or $k_2 = 18,000$ for one volt per cm. This agrees as well as could be expected with the theoretical value of k_2 for an electron

The term in H gives $\frac{V}{X} = 1.5 \times 10^{-5}$, so that since X was about 10^9 , $V = 1.5 \times 10^4$, which is about one hundred times too large. It is clear, therefore, that the part of the effect proportional to H is much greater than that to be expected theoretically. The reason for this discrepancy is not known, and further experiments are desirable to elucidate it.

It was found that when the electrodes at each end of the flame were removed, then the exploring wires took up a potential difference proportional to the magnetic field, and about equal to $200Hd$, where d is their distance apart. This indicates that the induced E.M.F. in the flame due to its upward motion has nearly the value VH per cm., as was to be expected.

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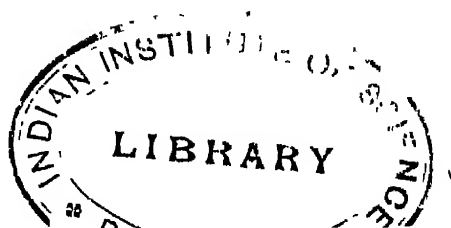
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